

Photocatalytic Treatment of Microcystin-LR-Containing Wastewater Using Pt/WO₃ Nanoparticles under Simulated Solar Light

Chao Zhao, Yingnan Yang, Zhenya Zhang*

Graduate School of Life and Environmental Science, University of Tsukuba, Tsukuba, Japan

Email: *zhang.zhenya.fu@u.tsukuba.ac.jp

Received April 7, 2012; revised May 10, 2012; accepted May 20, 2012

ABSTRACT

This study investigates the photocatalytic degradation of microcystin-LR (MC-LR) under simulated solar light using Pt modified nano-sized tungsten trioxides (Pt/WO₃). Photocatalytic activity was higher during the degradation of MC-LR with Pt/WO₃ than with pure WO₃ or TiO₂. The catalyst loading greatly affect the degradation performance. The rate of degradation is influenced by the initial pH of the reaction solution. This study also investigates the photocatalytic inactivation of cyanobacteria. The results show that the algal growth was successfully controlled by the Pt/WO₃. This study suggests Pt/WO₃ photocatalytic oxidation with solar light is a promising treatment for water containing MC-LR.

Keywords: Microcystin-LR; Photocatalytic Degradation; Solar Light; Tungsten Trioxide

1. Introduction

An intensification of agricultural and industrial activities resulting from an increase in population has led to eutrophication in superficial freshwater bodies and has therefore induced more frequent cyanobacteria blooms worldwide. The toxins released into freshwater by cyanobacteria are well-documented [1]. The most commonly occurring toxins released by cyanobacteria are called Microcystins.

Microcystins are a family of cyclic heptapeptides hepatotoxins containing the unique C₂₀ amino acid, 3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid, which is abbreviated Adda. The most abundant and frequently detected microcystin is microcystin-LR (MC-LR), which has leucine (L) and arginine (R) in the variable positions. Microcystins are strongly hepatotoxic because they disrupt protein phosphatases 1 and 2A [2], which may promote primary liver cancer and cause the death of animals and humans. The World Health Organization (WHO) has determined a provisional guideline value of 1.0 µg/L for MC-LR in drinking water.

Various water treatment processes have been evaluated to determine their efficacy in degrading these toxins because microcystins are considered a threat to human health. However, MCs are chemically stable across a range of pH values and temperatures, due to a cyclic

structure; consequently, traditional water treatment processes are unsuccessful in removing MCs [3-5].

Photocatalytic oxidation is an advanced oxidation technology that has been deemed an environmentally friendly water treatment option in recent years [6-10]. When a photocatalyst is illuminated with a light of an appropriate wavelength, pairs of electrons (e⁻) and electron holes (h⁺) are generated on the surface of the catalyst by photons. These pairs react with oxygen and water molecules or hydroxyl groups adsorbed on the surface of the catalyst and form highly reactive oxygen species, such as hydroxyl radicals (•OH), superoxide ions (•O₂⁻) or hydroperoxyl radicals (•OOH) [11]. Reactive oxygen species can nonselectively oxidize a large number of organic wastes, including dyes, pesticides, bacteria and herbicides [6-8,12]. Previous research proved that photocatalytic oxidation with TiO₂ photocatalyst could effectively destroy MCs, even at extremely high toxin concentrations [13,14]. However, TiO₂ has a large absorption band gap (E_g) of 3.2 eV that restricts its universal use because it can only absorb UV light [15]. Conversely, with an E_g between 2.4 eV and 2.8 eV, tungsten oxide (WO₃) is a photocatalyst that absorbs visible light irradiation up to 480 nm [11]. Compared with mixed metal oxides and doped oxides, WO₃ is inexpensive to prepare and stable in acidic and oxidative conditions, which makes it a promising material for photocatalytic applications. Previous research showed that WO₃ degradation of organic species under visible light intensified in the presence of

*Corresponding author.

suitable co-catalysts, such as Pt, Pd and CuO [16-18]. However, there is no literature on the photocatalytic degradation of MCs under visible light with WO₃-based catalysts.

The antimicrobial activity of photocatalytic reaction was first demonstrated by Matsunaga and coworkers [19], since then, photocatalysis has been shown to be capable of killing a wide range of organisms including Gram-negative and Gram-positive bacteria, including endospores, fungi, algae, protozoa and viruses, and has also been shown to be capable of inactivating prions [20-22]. Moreover recently works also reported that TiO₂-photocatalysis has the ability to inhibit the growth of the filamentous algae, *Oedogonium* and *Cladophora* [23,24].

In our study, the photocatalytic degradation of MC-LR, a model toxin, was investigated using Pt/WO₃ under simulated solar irradiation. Variations in sample parameters, such as catalyst loading and initial pH, were present in this study and are discussed later. To investigate the photocatalytic inactivation of cyanobacteria, *Microcystis aeruginosa* (*M. aeruginosa*) was selected as test species, for it is the most common blue-green algae and easily causes eutrophication.

2. Experimental

2.1. Chemicals and Preparation of Photocatalysts

MC-LR standard ($\geq 95\%$ purity; FW 995.2 g/mol) and WO₃ powder was purchased from Wako (Wako Pure Chemical Industries, Ltd., Japan). Sigma-Aldrich (Sigma-Aldrich Co. LLC., USA) supplied hexachloroplatinic acid (H₂PtCl₆·6H₂O). Ishihara (Ishihara Sangyo Ltd., Japan) supplied the nanoparticle compound TiO₂ (ST-21).

Pt-loaded WO₃ sample (Pt/WO₃) (0.5% w/w) was prepared by a photo deposition method [18]. An aqueous suspension containing the particulate WO₃ and H₂PtCl₆·6H₂O was exposed to visible light ($\lambda > 400$ nm) provided by a 300 W Xe lamp (LX-300F, Cermax, CA) fitted with a cutoff filter (L-42, HOYA, Japan). After 2 h of irradiation, methanol (10 vol%) was added and the suspension exposed to further irradiation for 2 h. The as-prepared sample was collected by centrifugation and washed twice with Milli-Q water and finally dried at 105°C for 2 h. The amount of deposited Pt was determined by analyzing the concentration of unused chloroplatinic acid remaining in the centrifuged solution after photo-deposition. The chloroplatinic acid concentration was analyzed by a inductively coupled plasma mass spectrometry (ICPS-8100, Shimadzu Co. Ltd., Japan). The prepared sample was characterized. UV-visible spectrum of the sample was recorded on a spectrophotometer (UV-2550, Shimadzu Co. Ltd., Japan). X-ray powder diffraction (XRD) measurement was carried out by using a X-ray diffractometer (Rigaku Smartlab).

2.2. Algal Culture

M. aeruginosa was obtained from National Institute for Environment Studies (NIES) (Ibaraki, Japan), The composition of the MA medium used in algal growth tests was listed in **Table 1**. 1 L of MA medium was added to a 3 L conical flask and was autoclaved at 121°C for 20 min. The cultivation was carried out in the cultivating box with illumination for 10 days. The continuous light was provided by a fluorescence lamp with an automated 12 h/12 h light/dark cycle. The light intensity during the light phase was 1500 lx. The temperature was controlled at 25°C \pm 1°C.

2.3. Photocatalytic Tests

The reactor was a 6-mL vessel equipped with a magnetic stirrer. A solar lamp (XC-100B, SERIC Ltd., Japan) was used as the irradiation source, and the light intensity was measured with a photometer (LI-250A, LI-COR Inc., USA). The photoemission spectrum was measured with an optical fiber spectrometer (USB4000, Ocean Optics Inc., USA).

An aliquot of stock MC-LR solution (50 mg/L) was added to the test solution to achieve an initial concentration of 1 mg/L. A suspension with catalyst particles was transferred to the reactor containing MC-LR to obtain a final volume of 5 ml. The catalyst loading was varied depending on the experiment condition. The initial pH was adjusted with H₂SO₄ or NaOH. Before irradiation, the suspension was stirred for 60 min in the dark to equilibrate the solution. During irradiation, samples were taken and centrifuged every 30 minutes for analysis.

Table 1. Composition of culture medium.

Component	Concentration (L ⁻¹)
Ca(NO ₃) ₂ ·4H ₂ O	50 mg
KNO ₃	100 mg
NaNO ₃	50 mg
Na ₂ SO ₄	40 mg
MgCl ₂ ·4H ₂ O	50 mg
β -Na ₂ glycerophosphate	100 mg
Na ₂ EDTA	5 mg
FeCl ₃ ·6H ₂ O	0.5 mg
MnCl ₂ ·4H ₂ O	5 mg
ZnCl ₂	0.5 mg
CoCl ₂ ·6H ₂ O	5 mg
Na ₂ MoO ₄ ·2H ₂ O	0.8 mg
H ₃ BO ₃	20 mg
Bicine	500 mg

Photocatalytic inhibition of *M. aeruginosa* was carried out in a 200-mL beaker equipped with a magnetic stirrer. The irradiation source was the same solar lamp with an automated 12 h/12 h light/dark cycle. All the experiment equipments were placed in a clean bench to prevent the interference of dust and microorganism brought by air. 150 ml of algal solution and a suspension with catalyst particles were added to the beaker for irradiation. Samples were taken every 2 days for analysis.

2.4. Detection of Hydroxyl Radicals ($\bullet\text{OH}$)

Photoluminescence (PL) with terephthalic acid as a probe molecule was used to detect $\bullet\text{OH}$ in the photocatalytic reaction system. Terephthalic acid reacts with $\bullet\text{OH}$ to produce highly fluorescent 2-hydroxyterephthalic acid [25].

In a beaker, a photocatalyst powder was dispersed in 20 mL of 5×10^{-4} M terephthalic acid aqueous solution and 2×10^{-3} M NaOH. The solar lamp was used as a light source. Samples were centrifuged every 20 min for analysis.

2.5. Analysis

The degradation of microcystin-LR was monitored by High-performance liquid chromatography (HPLC) (Jasco-1500, Jasco, Inc., Japan) with a high-resolution diode array detector (Jasco UV-1570) set at wavelength of 238 nm. Samples were separated on a C18 column (5 m, 250 mm, 4.6 mm id) using a mobile phase of acetonitrile and Milli-Q water containing 0.01 mol/L ammonium acetate (pH 6.8; 32:68 v/v) and a flow rate of 1 mL/min.

PL spectra generated by the 2-hydroxyterephthalic acid were measured on a Hitachi F-4500 fluorescence spectrophotometer set at a wavelength of 315 nm. The pH values of the solutions were measured with a pH meter (TES-1380, TES Co., Taiwan).

The growth of *M. aeruginosa* was evaluated by cells enumeration. The samples were diluted with Mill-Q water to obtain an appropriate cell density for microscopic

counts. Then the samples were dripped to a hemocytometer and covered with a clear cover for counting. The enumeration was achieved by a microscope.

3. Results and Discussion

3.1. Characterization of Photocatalyst Samples

Figure 1 shows the absorption (100-reflectance) spectra for WO_3 and Pt/WO_3 powders. The absorption of WO_3 increased at approximately 460 nm, which is consistent with previously reported value [16]. For Pt/WO_3 sample, with the contribution of Pt doping the spectrum shows stronger broad absorption in the visible light region. The XRD patterns of WO_3 and Pt/WO_3 samples are illustrated in **Figure 2**. Compared to tungsten oxide JCPD files (No. 43-1035) and those reported by others [23,24], the diffraction patterns of the samples assigned those of WO_3 monoclinic structure. As shown, no sign of crystallite Pt is detected in the patterns with Pt/WO_3 . It can be related to the fact that lower Pt concentrations lie below XRD instrumental detection limit and indicated that the Pt doping did not influence the crystal structures of WO_3 .

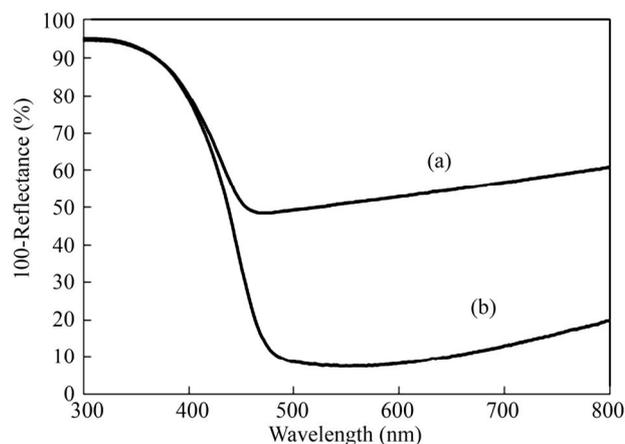


Figure 1. Absorption spectrum of (A) Pt/WO_3 and (B) Pure WO_3 , respectively.

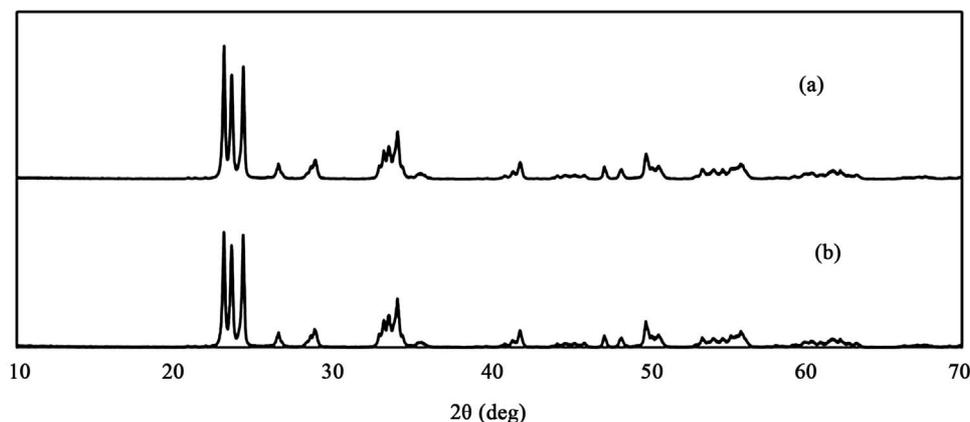


Figure 2. XRD patterns of (a) pure WO_3 and (b) Pt/WO_3 , respectively.

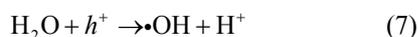
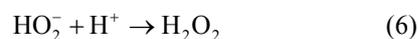
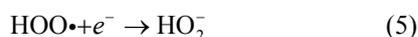
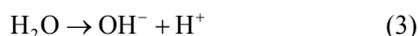
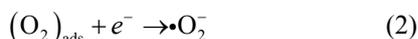
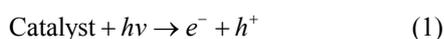
3.2. Photocatalytic Degradation of MC-LR with Pt/WO₃

As shown in **Figure 3**, the concentration of MC-LR was virtually unchanged after 3 h of irradiation when there was no photocatalyst in the solution, thereby indicating MC-LR was stable under solar irradiation. After 3 h of irradiation, 19% of MC-LR was removed from a solution with only TiO₂ added, and 24% of MC-LR was removed from a solution in which only WO₃ was added. Compare to pure TiO₂ and WO₃, the performance of modified WO₃ was much better, with 3 h of irradiation. Over 81% of MR-LR was degraded by the Pt/WO₃ composite within 90 min. Furthermore, the removal efficacy was 100% when the contact time was lengthened to 180 min.

Poor MC-LR removal efficiency by a solution containing only TiO₂ was attributable to the light source. The simulated solar lamp used in this experiment emitted light mainly with wavelengths greater than 400 nm, and the TiO₂ excitation range is less than 390 nm [15]. The low photocatalytic activity of pure WO₃ is because the conduction band level of WO₃ (+0.5V vs. NHE) is more positive than the potential for the single-electron reduction of oxygen (O₂/O₂⁻ = -0.56 V vs. NHE; O₂/HO₂⁻ = -0.13 V vs. NHE) [17]. Without co-catalysts, the high conduction band of WO₃ restricts the compound's activity with an organic compound [10].

3.3. Photocatalytic Degradation Mechanism

Pt is a co-catalysts for WO₃-induced photocatalytic reactions that can promote O₂ reduction in a multi-electron process [17,26]. In a photocatalytic reaction, the following chain reactions have been postulated [11]:



Several highly reactive oxygen species, such as $\cdot\text{OH}$, $\text{HOO}\cdot$ and $\cdot\text{O}_2^-$, are generated through the reduction of O₂ to oxidized organic compounds. Accordingly, organic compounds could be effectively degraded by WO₃ in the presence of a co-catalyst.

Photocatalytic degradation of MC-LR was initiated by

the attack of hydroxyl radical on the conjugated diene structure of Adda [27], thereby indicating the primary reactive species in MC-LR degradation was the hydroxyl radical. Kim et al. proved that the deposition of Pt on WO₃ facilitates the generation of OH radicals under visible light [28], and our experiments confirmed this phenomenon using photoluminescence (PL). **Figure 4** shows the spectra observed during irradiation of the Pt/WO₃ sample. At approximately 425 nm, PL intensity gradually increased with an increase in irradiation time, thereby suggesting that OH radicals are formed on the photocatalyst-water interface via photocatalytic reactions [25,29]. Because the photocatalytic degradation of MC-LR was initiated by an OH radical [27], Pt/WO₃ is particularly effective in the photocatalytic degradation of MC-LR.

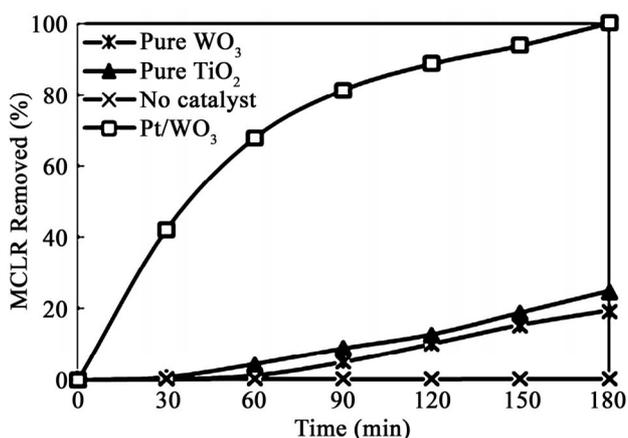
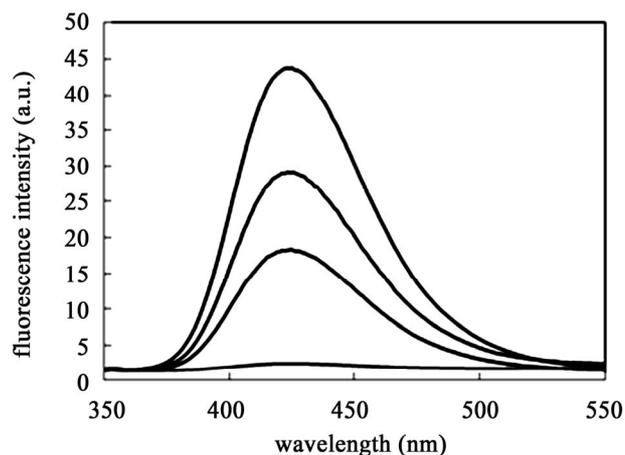


Figure 3. The effect of catalysts on the efficiency of photocatalytic degradation of MC-LR. Experimental conditions: MC-LR concentration of 1 mg/L, catalyst concentration of 100 mg/L and simulated solar light intensity of 0.4 mW/cm².



Experimental conditions: NaOH concentration of 2×10^{-3} M, terephthalic acid concentration of 5×10^{-4} M, Pt/WO₃ concentration of 200 mg/L and simulated solar light intensity of 0.4 mW/cm².

Figure 4. PL spectral changes observed during irradiation of the Pt/WO₃ sample.

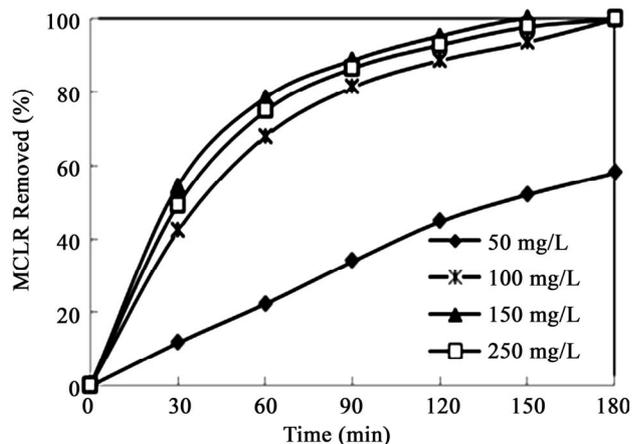
3.4. Effect of Catalyst Loading

Experiments were carried out by varying the catalyst concentration from 50 to 250 mg/L. The results are shown in **Figure 5**. When the catalyst loading was 50 mg/L, the degradation efficiency was low, only 58% of MC-LR was removed after 3 h irradiation. The increase in the catalyst loading from 50 to 150 mg/L sharply increased the degradation efficiency. However, when the catalyst loading further increased to 250 mg/L, the degradation efficiency decreased. The results indicate that the inactivation efficiency is not proportional to the catalyst loading. The increasing catalyst loading induces an increase in the availability of active sites on the catalyst surface and produces a proportional increase in the number of active radicals by absorbing photons. However, an increase in the catalyst concentration results in increasing the light source extinction coefficient, and subsequently reducing the reaction efficiency [21,30]. Based on this result, 150 mg/L was chosen as the optimum catalyst loading.

3.5. The Effect of Initial pH on the Photocatalytic Degradation of MC-LR

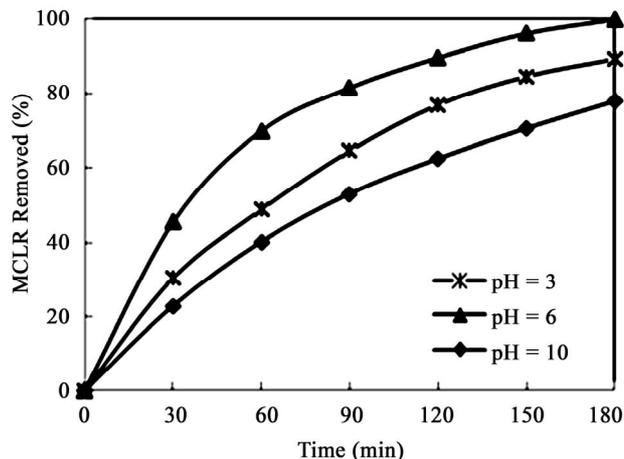
The pH affects the surface condition of catalysts and MC-LR and the generation of hydroxyl radical in hydroxylation reactions. After 180 min of irradiation, the removal of MC-LR was 89%, 100% and 77% with pH values of 3, 6 and 10, respectively (**Figure 6**).

Although the degradation of MC-LR was initiated by the attack of hydroxyl radical [27], the number of $\bullet\text{OH}$ ions should be lower at an acidic pH because hydronium ions favor the presence of an electron hole (Equation (8)) [31]. At low pH, MC-LR degradation would be adversely affected due to the lack of OH^- ions. The initial pH was



Experimental conditions: MC-LR concentration of 1 mg/L, simulated solar light intensity of 0.4 mW/cm^2 .

Figure 5. Efficiency of photocatalytic degradation of MC-LR as a function of catalyst loading.



Experimental conditions: MC-LR concentration of 1 mg/L, Pt/WO_3 concentration of 100 mg/L and simulated solar light intensity of 0.4 mW/cm^2 .

Figure 6. Efficiency of photocatalytic degradation of MC-LR as a function of initial pH.

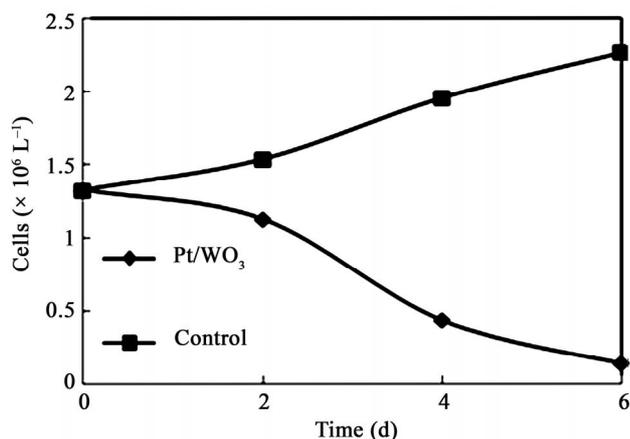
adjusted by H_2SO_4 , but Liang *et al.* reported that SO_4^{2-} ions have an adverse effect on the photocatalytic degradation rate [32]. Given the evidence, we can explain the lower efficiency observed in our experiment at acid pH.

The point of zero zeta-potential (PZZP) for WO_3 occurs at approximately pH 2, and WO_3 particles are negatively charged when the pH of a solution is greater than 2 [28]. At pH values between 3 and 12, the carboxylic groups of MC-LR are ionized, and the molecule is negatively charged [33]. In basic conditions, negatively charged WO_3 molecules repel MC-LR and inhibit interactions between the toxins and the catalysts. Fewer interactions result in lower photocatalytic activity and a lower degradation rate. Our results are consistent with a study by Lawton *et al.* in which the reaction rate of photocatalytic degradation of MC-LR by TiO_2 was lowest at pH 10 [34].

3.6. Photocatalytic Inhibition of Algal Growth under Solar Light

Figure 7 shows the results of photocatalytic inhibition of algal growth under solar light. After 6 days of irradiation, *M. aeruginosa* in the control samples kept growing and the number of algae cells increased from 1.3×10^6 to 2.2×10^6 . However, the growth of *M. aeruginosa* in the samples treated by photocatalyst was inhibited and the algae cells decreased from 1.3×10^6 to 0.1×10^6 . These results show that the photocatalytic treatment had the function of inactivation of microorganisms.

It is generally believed that the inactivation of microorganisms by photocatalytic treatment is mainly due to oxidative radicals (mainly $\bullet\text{OH}$) produced by photocatalyst irradiation [35].



Experimental conditions: Catalyst concentration of 150 mg/L and simulated solar light intensity of 0.8 mW/cm².

Figure 7. Photocatalytic inhibition of algal growth.

4. Conclusions

Under simulated solar irradiation, WO₃ degrades MC-LR more effectively in the presence of co-catalyst compared to solutions with pure TiO₂ or pure WO₃. The highest rate of MC-LR removal occurred in solutions containing Pt/WO₃. Specifically, 1 mg/L of MC-LR was removed after 3 h of irradiation by 100 mg/L of Pt/WO₃. The optimum catalyst loading was 150 mg/L. A neutral pH, such as a pH of 6, improved the efficacy of toxin removal. The experiment results show that the algal growth was successfully controlled by the Pt/WO₃.

5. Acknowledgements

This work was supported in part by Grant-in-Aid for Research Activity Start-up 22880007 and Scientific Research (A) 22248075 from Japan Society for the Promotion of Science (JSPS).

REFERENCES

- [1] F. Al Momani, D. W. Smith and M. G. El-Din, "Degradation of Cyanobacteria Toxin by Advanced Oxidation Processes," *Journal of Hazardous Materials*, Vol. 150, No. 2, 2008, pp. 238-249. [doi:10.1016/j.jhazmat.2007.04.087](https://doi.org/10.1016/j.jhazmat.2007.04.087)
- [2] R. E. Honkanen, J. Zwiller, R. E. Moore, S. L. Daily, B. S. Khatra and M. Dukelow, A. L. Boynton, "Characterization of Microcystin-LR, a Potent Inhibitor of Type-1 and Type-2A Protein Phosphatases," *Journal of Biological Chemistry*, Vol. 265, No. 32, 1990, pp. 19401-19404.
- [3] V. M. Vasconcelos and E. Pereira, "Cyanobacteria Diversity and Toxicity in a Wastewater Treatment Plant (Portugal)," *Water Research*, Vol. 35, No. 5, 2001, pp. 1354-1357. [doi:10.1016/S0043-1354\(00\)00512-1](https://doi.org/10.1016/S0043-1354(00)00512-1)
- [4] K. Himberg, A. M. Keijola, L. Hiisvirta, H. Pyysalo and K. Sivonen, "The Effect of Water Treatment Processes on the Removal of Hepatotoxins from Microcystin and Oscillatoria Cyanobacteria: A Laboratory Study," *Water Research*, Vol. 23, No. 8, 1989, pp. 979-984. [doi:10.1016/0043-1354\(89\)90171-1](https://doi.org/10.1016/0043-1354(89)90171-1)
- [5] S. Takenaka and Y. Tanaka, "Behavior of Microcystins and Its Decomposition Product in Water Treatment Process," *Chemosphere*, Vol. 31, No. 7, 1995, pp. 3635-3641. [doi:10.1016/0045-6535\(95\)00212-Q](https://doi.org/10.1016/0045-6535(95)00212-Q)
- [6] C. Shifu and C. Gengyu, "Photocatalytic Degradation of Organophosphorus Pesticides Using Floating Photocatalyst TiO₂-SiO₂/Beads by Sunlight," *Solar Energy*, Vol. 79, No. 1, 2005, pp. 1-9. [doi:10.1016/j.solener.2004.10.006](https://doi.org/10.1016/j.solener.2004.10.006)
- [7] M. Sharon, B. Pal and D. V. Kamat, "Photocatalytic Killing of Pathogenic Bacterial Cells Using Nanosize Fe₂O₃ and Carbon Nanotubes," *Journal of Biomedical Nanotechnology*, Vol. 1, No. 3, 2005, pp. 365-368. [doi:10.1166/jbn.2005.034](https://doi.org/10.1166/jbn.2005.034)
- [8] M. Canle, M. I. Fernandez, S. Rodriguez, J. A. Santaballa, S. Steenken and E. Vulliet, "Mechanisms of Direct and TiO₂-Photocatalysed UV Degradation of phenylurea Herbicides," *Chemphyschem*, Vol. 6, No. 10, 2005, pp. 2064-2074. [doi:10.1002/cphc.200500004](https://doi.org/10.1002/cphc.200500004)
- [9] T. Arai, M. Yanagida, Y. Konishi, Y. Iwasaki, H. Sugihara and K. Sayama, "Efficient Complete Oxidation of Acetaldehyde into CO₂ over CuBi₂O₄/WO₃ Composite Photocatalyst under Visible and UV Light Irradiation," *Journal of Physical Chemistry C*, Vol. 111, No. 21, 2007, pp. 7574-7577. [doi:10.1021/jp0725533](https://doi.org/10.1021/jp0725533)
- [10] M. Miyauchi, "Photocatalysis and photoinduced hydrophilicity of WO₃ thin films with underlying Pt nanoparticles," *Physical Chemistry Chemical Physics*, Vol. 10, No. 41, 2008, pp. 6258-6265. [doi: 10.1039/b807426g](https://doi.org/10.1039/b807426g)
- [11] U. I. Gaya and A. H. Abdullah, "Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems," *Journal of Photochemistry and Photobiology C-Photochemistry Reviews*, Vol. 9, No. 1, 2008, pp. 1-12. [doi:10.1016/j.jphotochemrev.2007.12.003](https://doi.org/10.1016/j.jphotochemrev.2007.12.003)
- [12] N. Genc, "Photocatalytic Oxidation of a reactive Azo Dye and Evaluation of the Biodegradability of Photocatalytically Treated and Untreated Dye," *Water SA*, Vol. 30, No. 3, 2004, pp. 399-405. [doi:10.4314/wsa.v30i3.5089](https://doi.org/10.4314/wsa.v30i3.5089)
- [13] L. A. Lawton, P. K. J. Robertson, B. Cornish and M. Jaspars, "Detoxification of Microcystins (Cyanobacterial Hepatotoxins) Using TiO₂ Photocatalytic Oxidation," *Environmental Science & Technology*, Vol. 33, No. 5, 1999, pp. 771-775. [doi:10.1021/es9806682](https://doi.org/10.1021/es9806682)
- [14] I. Liu, L. A. Lawton, D. W. Bahnemann and P. K. J. Robertson, "The Photocatalytic Destruction of the Cyanotoxin, Nodularin Using TiO₂," *Applied Catalysis B: Environmental*, Vol. 60, No. 3-4, 2005, pp. 245-252. [doi:10.1016/j.apcatb.2005.03.006](https://doi.org/10.1016/j.apcatb.2005.03.006)
- [15] Z. G. Zhao and M. Miyauchi, "Nanoporous-Walled Tungsten Oxide Nanotubes as Highly Active Visible-Light-Driven Photocatalysts," *Angewandte Chemie: International Edition*, Vol. 47, No. 37, 2008, pp. 7051-7055. [doi:10.1002/anie.200802207](https://doi.org/10.1002/anie.200802207)
- [16] R. Abe, H. Takami, N. Murakami and B. Ohtani, "Pristine Simple Oxides as Visible Light Driven Photocatalysts: Highly Efficient Decomposition of Organic Compounds over Platinum-Loaded Tungsten Oxide," *Journal*

- of the American Chemical Society, Vol. 130, No. 25, 2008, pp. 7780-7781. [doi:10.1021/ja800835q](https://doi.org/10.1021/ja800835q)
- [17] T. Arai, M. Horiguchi, M. Yanagida, T. Gunji, H. Sugihara and K. Sayama, "Complete Oxidation of Acetaldehyde and Toluene over a Pd/WO₃ Photocatalyst under Fluorescent- or Visible-Light Irradiation," *Chemical Communications*, Vol. No. 43, 2008, pp. 5565-5567.
- [18] T. Arai, M. Yanagida, Y. Konishi, Y. Iwasaki, H. Sugihara and K. Sayama, "Promotion Effect of CuO Co-Catalyst on WO₃-Catalyzed Photo Degradation of Organic Substances," *Catalysis Communications*, Vol. 9, No. 6, 2008, pp. 1254-1258. [doi:10.1016/j.catcom.2007.11.012](https://doi.org/10.1016/j.catcom.2007.11.012)
- [19] T. Matsunaga, R. Tomoda, T. Nakajima and H. Wake, "Photoelectrochemical Sterilization of Microbial Cells by Semiconductor Powders," *FEMS Microbiology Letters*, Vol. 29, No. 1-2, 1985, pp. 211-214. [doi:10.1111/j.1574-6968.1985.tb00864.x](https://doi.org/10.1111/j.1574-6968.1985.tb00864.x)
- [20] J. A. Ibanez, M. I. Litter and R. A. Pizarro, "Photocatalytic Bactericidal Effect of TiO₂ on Enterobacter Cloacae. Comparative Study with Other Gram (-) Bacteria," *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 157, No. 1, 2003, pp. 81-85.
- [21] M. N. Chong, B. Jin, H. Zhu and C. Saint, "Bacterial Inactivation Kinetics, Regrowth and Synergistic Competition in a Photocatalytic Disinfection System Using Anatase Titanate Nanofiber Catalyst," *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 214, No. 1, 2010, pp. 1-9. [doi:10.1016/j.jphotochem.2010.05.018](https://doi.org/10.1016/j.jphotochem.2010.05.018)
- [22] B. Kim, D. Kim, D. Cho and S. Cho, "Bactericidal Effect of TiO₂ Photocatalyst on Selected Food-Borne Pathogenic Bacteria," *Chemosphere*, Vol. 52, No. 1, 2003, pp. 277-281. [doi:10.1016/S0045-6535\(03\)00051-1](https://doi.org/10.1016/S0045-6535(03)00051-1)
- [23] C. A. Linkous, G. J. Carter, D. B. Locuson, A. J. Ouellette, D. K. Slattery and L. A. Smitha, "Photocatalytic Inhibition of Algae Growth Using TiO₂, WO₃, and Cocatalyst Modifications," *Environmental Science & Technology*, Vol. 34, No. 22, 2000, pp. 4754-4758. [doi:10.1021/es001080+](https://doi.org/10.1021/es001080+)
- [24] J. R. Peller, R. L. Whitman, S. Griffith, P. Harris, C. Peller and J. Scalzitti, "TiO₂ as a Photocatalyst for Control of the Aquatic Invasive Alga, Cladophora, under Natural and Artificial Light," *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 186, No. 2-3, 2007, pp. 212-217. [doi:10.1016/j.jphotochem.2006.08.009](https://doi.org/10.1016/j.jphotochem.2006.08.009)
- [25] K.-i. Ishibashi, A. Fujishima, T. Watanabe and K. Hashimoto, "Detection of Active Oxidative Species in TiO₂ Photocatalysis Using the Fluorescence Technique," *Electrochemistry Communications*, Vol. 2, No. 3, 2000, pp. 207-210. [doi:10.1016/S1388-2481\(00\)00006-0](https://doi.org/10.1016/S1388-2481(00)00006-0)
- [26] T. Arai, M. Horiguchi, M. Yanagida, T. Gunji, H. Sugihara and K. Sayama, "Reaction Mechanism and Activity of WO₃-Catalyzed Photodegradation of Organic Substances Promoted by a CuO Cocatalyst," *Journal of Physical Chemistry C*, Vol. 113, No. 16, 2009, pp. 6602-6609. [doi:10.1021/jp811134z](https://doi.org/10.1021/jp811134z)
- [27] I. Liu, L. A. Lawton and P. K. J. Robertson, "Mechanistic Studies of the Photocatalytic Oxidation of Microcystin-LR: An Investigation of Byproducts of the Decomposition Process," *Environmental Science & Technology*, Vol. 37, No. 14, 2003, pp. 3214-3219. [doi:10.1021/es0201855](https://doi.org/10.1021/es0201855)
- [28] J. Kim, C. W. Lee and W. Choi, "Platinized WO₃ as an Environmental Photocatalyst that Generates OH Radicals under Visible Light," *Environmental Science & Technology*, Vol. 44, No. 17, 2010, pp. 6849-6854. [doi:10.1021/es101981r](https://doi.org/10.1021/es101981r)
- [29] Q. Xiao, Z. Si, J. Zhang, C. Xiao and X. Tan, "Photoinduced Hydroxyl Radical and Photocatalytic Activity of Samarium-Doped TiO₂ Nanocrystalline," *Journal of Hazardous Materials*, Vol. 150, No. 1, 2008, pp. 62-67. [doi:10.1016/j.jhazmat.2007.04.045](https://doi.org/10.1016/j.jhazmat.2007.04.045)
- [30] B. Neppolian, H. C. Choi, S. Sakthivel, B. Arabindoo and V. Murugesan, "Solar Light Induced and TiO₂ Assisted Degradation of Textile Dye Reactive Blue 4," *Chemosphere*, Vol. 46, No. 8, 2002, pp. 1173-1181. [doi:10.1016/S0045-6535\(01\)00284-3](https://doi.org/10.1016/S0045-6535(01)00284-3)
- [31] L. Elsellami, F. Vocanson, F. Dappozze, E. Puzenat, O. Paisse, A. Houas and C. Guillard, "Kinetic of Adsorption and of Photocatalytic Degradation of Phenylalanine Effect of pH and Light Intensity," *Applied Catalysis A: General*, Vol. 380, No. 1-2, 2010, pp. 142-148. [doi:10.1016/j.apcata.2010.03.054](https://doi.org/10.1016/j.apcata.2010.03.054)
- [32] H.-C. Liang, X.-Z. Li, Y.-H. Yang and K.-H. Sze, "Effects of dissolved Oxygen, pH, and Anions on the 2,3-Dichlorophenol Degradation by Photocatalytic Reaction with Anodic TiO₂ Nanotube Films," *Chemosphere*, Vol. 73, No. 5, 2008, pp. 805-812. [doi:10.1016/j.chemosphere.2008.06.007](https://doi.org/10.1016/j.chemosphere.2008.06.007)
- [33] M. G. Antoniou, J. A. Shoemaker, A. A. de la Cruz and D. D. Dionysiou, "LC/MS/MS Structure Elucidation of Reaction Intermediates Formed during the TiO₂ Photocatalysis of Microcystin-LR," *Toxicol*, Vol. 51, No. 6, 2008, pp. 1103-1118. [doi:10.1016/j.toxicol.2008.01.018](https://doi.org/10.1016/j.toxicol.2008.01.018)
- [34] L. A. Lawton, P. K. J. Robertson, B. Cornish, I. L. Marr and M. Jaspars, "Processes Influencing Surface Interaction and Photocatalytic Destruction of Microcystins on Titanium Dioxide Photocatalysts," *Journal of Catalysis*, Vol. 213, No. 1, 2003, pp. 109-113. [doi:10.1016/S0021-9517\(02\)00049-0](https://doi.org/10.1016/S0021-9517(02)00049-0)
- [35] L. Rizzo, "Inactivation and Injury of Total Coliform Bacteria after Primary Disinfection of Drinking Water by TiO₂ Photocatalysis," *Journal of Hazardous Materials*, Vol. 165, No. 1-3, 2009, pp. 48-51. [doi:10.1016/j.jhazmat.2008.09.068](https://doi.org/10.1016/j.jhazmat.2008.09.068)