

Degradation of Microcystin-RR by Combination of UV/H₂O₂ Technique

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Abstract: The experiments were performed to investigate the degradation of microcystins in order to assess the effectiveness and feasibility of UV/H₂O₂ system for the disinfection of water polluted by microcystins. The influence factors such as H₂O₂, pH and UV light intensities were investigated respectively. Degradation of microcystin-RR (MC-RR) could be fitted by either the pseudo-first-order or second-order rate equations. This homogenous system could significantly enhance the degradation rate due to the synergetic effect between UV and H₂O₂. The degradation mainly followed the mechanism of direct photolysis and ·OH oxidation reactions. Experimental results showed that 94.83% of MC-RR was removed under optimal experimental conditions and the UV/H₂O₂ system provided an alternative to promote the removal of microcystins in drinking water supplies.

Keywords: Microcystin-RR, degradation, kinetics, UV/H₂O₂ photo-oxidation.

Microcystins are cyclic hepatotoxic peptides produced by freshwater *cyanobacteria* such as *Microcystis*, *Oscillatoria*, *Nostoc*, *Aphanizomenon* and *Anabaena*¹. They are hardly degraded by conventional water treatment processes and harmful to human health².

Coagulation/flocculation, activated carbon adsorption or membrane techniques can only transfer, more or less selectively, microcystins from one phase to another, finally leaving the environmental problem unsolved³. Therefore, it is necessary to develop novel systems for MC-RR destruction leading to complete mineralization or to less harmful compounds.

The advanced oxidation processes (AOPs) provide promising treatment options for microcystins-containing water^{4,5}. The UV/H₂O₂ photo-oxidation, which involves the production of reactive species, especially the hydroxyl radicals (·OH), is an example of AOPs. It is capable of oxidizing organic contaminants in water⁶. In comparison with other AOPs, such as Fenton, UV/O₃, UV/TiO₂, *etc.*, UV/H₂O₂ system shows some advantages: no phase transfer and sludge formation, no secondary pollution, simplicity of operation and low investment costs, *etc.*. However, degradation of microcystins with this process was seldom reported in literatures. In the present study, the degradation of MC-RR (as a target of microcystins) was investigated by UV/H₂O₂ technique.

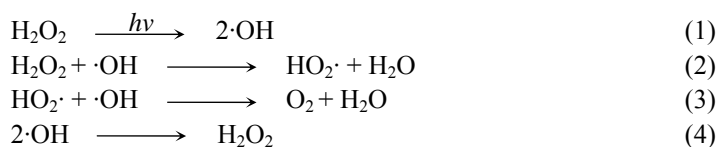
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Methods

Under continuous magnetic stirring in a 0.5 L photo-reactor, 0.72 mg/L MC-RR was irradiated by UV₂₅₄ light after adding calculated H₂O₂. Reaction temperature was maintained at 25±1°C by a water circulator. At predefined times, samples were analyzed by solid phase extraction-high performance liquid chromatograph (SPE-HPLC) method⁷.

Results and Discussion

Effect of H₂O₂ concentrations on the degradation of MC-RR was shown in **Figure 1**. At lower H₂O₂ concentrations, degradation of MC-RR improved significantly with increasing H₂O₂ concentrations. However, the degradation would be retarded obviously after increasing the H₂O₂ concentration above 1 mmol/L, and then the degradation rate increased slightly. Those results could be explained by the following reactions:



It has been proved that hydrogen peroxide acts as both promoter and scavenger of hydroxyl radicals⁸. Hydrogen peroxide can generate $\cdot\text{OH}$ under UV irradiation. Additionally, H₂O₂ reacts with the $\cdot\text{OH}$ to form hydroperoxyl radical⁹, which has lower oxidative capability compared with $\cdot\text{OH}$. Scavenging action of H₂O₂ in high concentrations would inhibit the propagation of $\cdot\text{OH}$, and then reduce its oxidative capability.

Effect of pH on the degradation of MC-RR was presented in **Figure 2**. The results showed that the degradation rate increased when pH increased from 5 to 8.1. Conversely, degradation rate reduced when pH value was higher than 9.

Increase in pH could improve the formation of hydroperoxide anion (HO₂⁻) to generate more $\cdot\text{OH}$, since the molar extinction coefficient of HO₂⁻ (240 mol⁻¹·L·s⁻¹) was higher than that of H₂O₂ (19.6 mol⁻¹·L·s⁻¹)¹⁰, and the reaction rate of HO₂⁻ reacted with $\cdot\text{OH}$ was faster than that of H₂O₂ did¹¹. At the same time, the degradation product CO₂ easily changed to the bicarbonate and carbonate anions after dissolving in water, especially at high pH. However, HO₂⁻, CO₃²⁻ and HCO₃⁻ were also scavengers of $\cdot\text{OH}$ through the following reactions¹². Therefore, scavenging rate of $\cdot\text{OH}$ increased markedly with increasing solution pH.

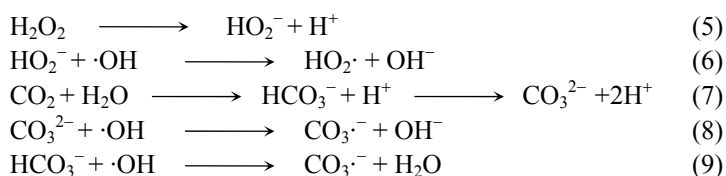
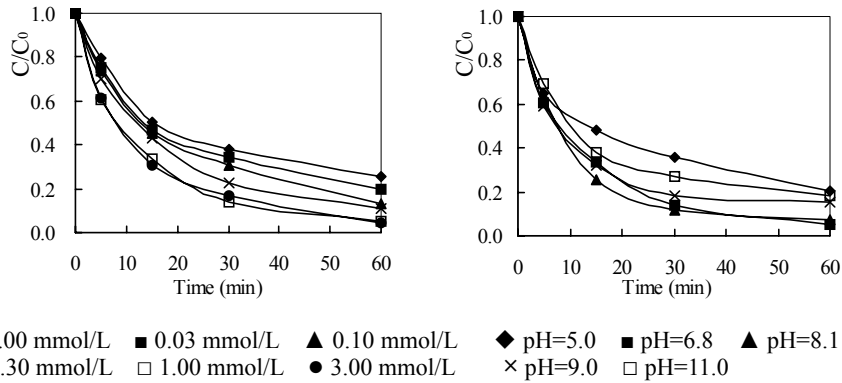


Figure 1 Effect of initial concentration of H₂O₂ **Figure 2** Effect of initial aqueous solution pH



UV light intensity significantly improved the degradation of MC-RR compared with dark reaction (**Figure 3**). Increasing of light intensity was favourable to decompose H₂O₂ to generate more ·OH and also enhance the UV photolysis capability. Consequently, the two actions would contribute significantly to destruct MC-RR. However, the light intensity was not directly proportional to the degradation rate of MC-RR as shown in **Figure 3**.

The degradation of MC-RR by UV/H₂O₂, UV and H₂O₂ processes were illustrated in **Figure 4**. As observed, MC-RR was found to be refractory to oxidize with H₂O₂ applied alone. UV direct photolysis was more available than individual H₂O₂ treatment. Furthermore, the presence of H₂O₂ significantly increased the degradation rate of MC-RR compared with UV photolysis.

Based on the pseudo-first-order and second-order rate equations, the observed kinetic parameters were calculated and listed in **Table 1**. The results showed that the degradation of MC-RR could be fitted well with both pseudo-first-order and second-order rate equations. From the rate constants, it could also be concluded that there existed synergetic effect between UV photolysis and H₂O₂ oxidation.

Figure 3 Effect of UV light intensity

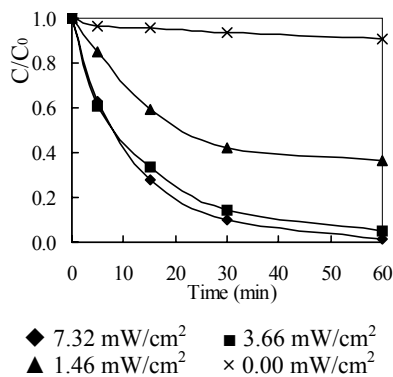


Figure 4 Effect of different processes

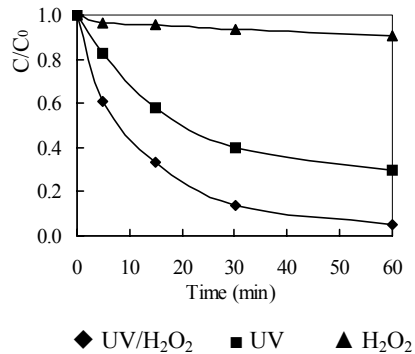


Table 1 Degradation kinetic parameters of MC-RR in different oxidation processes

System	Pseudo-first-order kinetics			Second-order kinetics		
	rate equation	k_1, min^{-1}	R^2	rate equation	$k_2, \text{mg}^{-1}\cdot\text{L}\cdot\text{min}^{-1}$	R^2
UV/H ₂ O ₂	$\ln(C_0/C)=0.0538t$	0.0538	0.9412	$1/C-1/C_0=0.3855t$	0.3855	0.9444
UV	$\ln(C_0/C)=0.0231t$	0.0231	0.8703	$1/C-1/C_0=0.0582t$	0.0582	0.9719
H ₂ O ₂	$\ln(C_0/C)=0.0018t$	0.0018	0.7833	$1/C-1/C_0=0.0026t$	0.0026	0.8044

As mentioned above, UV/H₂O₂ system was effective in decomposing MC-RR in aqueous solution. The degradation of MC-RR was strongly accelerated in this system because of the synergetic effect of H₂O₂ and UV irradiation. UV photolysis and ·OH were responsible for the degradation of MC-RR. After reacting for 60 min, 94.83% of MC-RR was removed under optimal experimental conditions.

Acknowledgments

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References

1. E. Ito, A. Takai, F. Kondo, H. Masui, S. Imanishi, K. I. Harada, *Toxicon*, **2002**, *40*, 1017.
2. I. R. Falconer, *Phycologia*, **2001**, *40*, 228.
3. C. W. K. Chow, M. Drikas, J. House, *et al.*, *Water Res.*, **1999**, *33*, 3253.
4. L. A. Lawton, P. K. J. Robertson, B. J. P. A. Cornish, *et al.*, *J. Catal.*, **2003**, *213*, 109.
5. K. Tsuji, S. Naito, F. Kondo, *et al.*, *Environ. Sci. Technol.*, **1994**, *28*, 173.
6. W. H. Glaze, Y. Lay, J. W. Kang, *Ind. Eng. Chem. Res.*, **1995**, *34*, 2314.
7. L. A. Lawton, C. Edwardas, G. A. Codd, *Analyst*, **1994**, *119*, 1525.
8. W. H. Glaze, J. W. Kang, D. H. Chapin, *Ozone Sci. Eng.*, **1987**, *9*, 335.
9. J. C. Crittenden, S. Hu, D. W. Hand, S.A. Green, *Water Res.*, **1999**, *33*, 2315.
10. F. J. Beltran, G. Ovejero, J. Rivas, *Ind. Eng. Chem. Res.*, **1996**, *35*, 883.
11. G. V. Buxton, A. J. Elliot, *Radiat. Phys. Chem.*, **1986**, *27*, 241.
12. G. R. Peyton, W. H. Glaze, *Environ. Sci. Technol.*, **1988**, *22*, 761.

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