

富里酸 (FA) 对 MC-LR 的光敏降解作用及相关环境条件研究

Photosensitized degradation of MC-LR by fulvic acid (FA) and its related environmental conditions

WANG Yanzhao, ZHANG Jingjing, ZHANG Dajuan, DAI Wei, BI Xiangdong

(Key Laboratory of Aqua-ecology and Aquaculture of Tianjin, College of Fisheries Sciences, Tianjin Agricultural University, Tianjin 300384, China)

Abstract

Cyanobacteria bloom frequently occurs in freshwater ponds, and microcystins (MCs) can cause direct harm to farmed animals. Photodegradation is an effective way to reduce MCs-caused harm in natural waters. Fulvic acid (FA) is a widely existing photosensitizer in ponds. Effects of different concentrations of FA on the photosensitized degradation of MC-LR and its related environment conditions were investigated under simulated solar light. The results showed that the direct photolysis of MC-LR occurred in deionized water. Different concentrations (2.5, 5, 7.5 and 10 mg L⁻¹) of FA promoted the photolysis of MC-LR, of which 7.5 mg L⁻¹FA had the best photosensitized degradation effect. The degradation rate reached 52.65% after 180 min. The photosensitive degradation of MC-LR by FA conformed to the second-order reaction kinetics, and the photosensitive degradation products are the same as the direct photolysis products in deionized water. Under different pH values and light intensities, the photosensitive degradation effects of FA on MC-LR were pH6>pH7>pH8>pH9 and 350 W>500 W>200 W, respectively. The results showed that both pH value and light intensity affected the photosensitized degradation of FA on MC-LR.

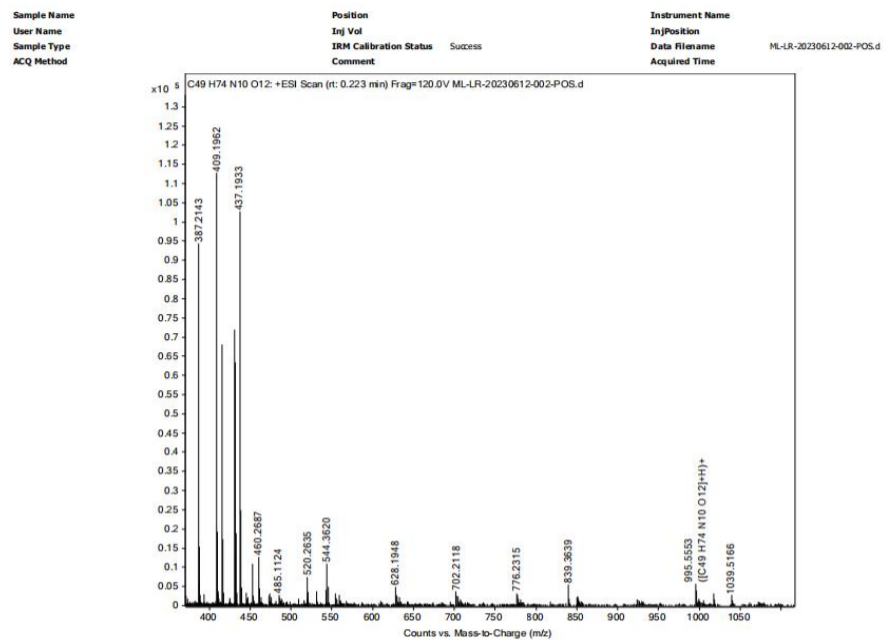


Fig.1 Mass spectrum of MC-LR

Methodology

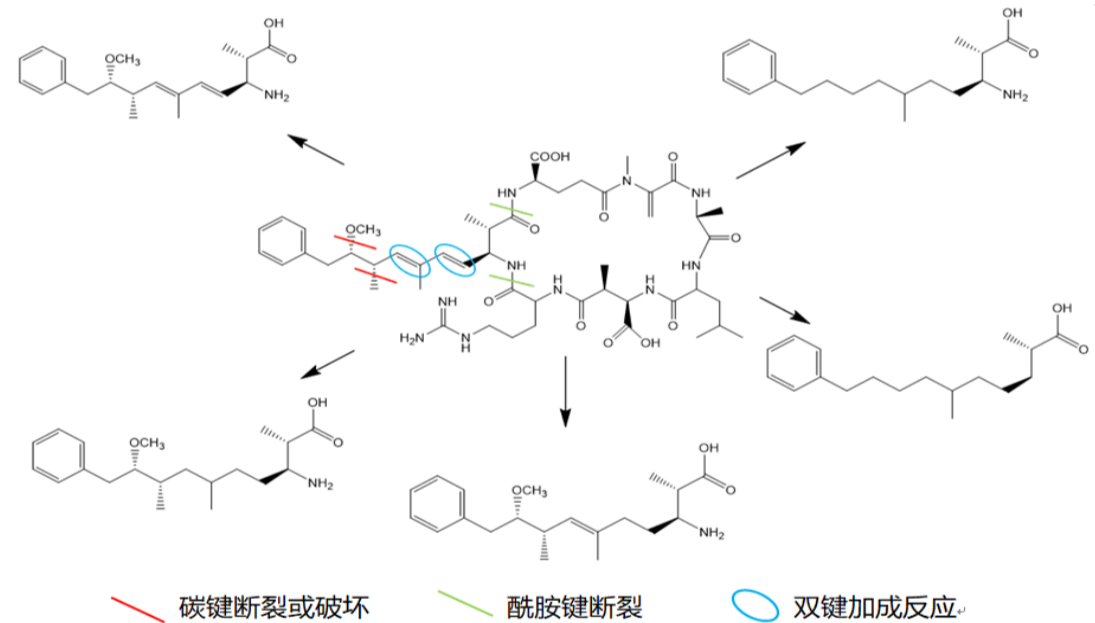
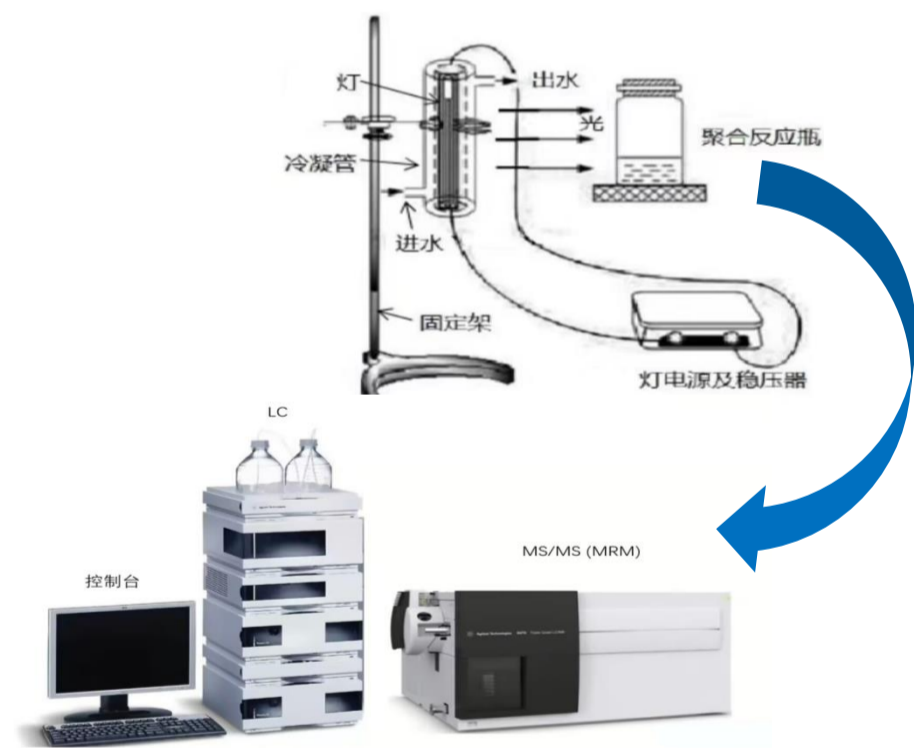


Fig.2 Photolysis products of MC-LR in different concentrations of FA solution

在 7.5 mg L⁻¹FA 溶液中, MC-LR 光降解产物的 m/z 值为 277.2156、292.2267、332.2190、334.2349、336.2518, 去离子水中 m/z 值为 277.2159, 292.2267, 332.2192, 334.2350, 336.2517。FA 溶液中 MC-LR 的降解产物与去离子水中的基本相同。根据不同产物的 (M+H)⁺m/z 数据推断产物结构及可能的降解途径见图 2, 以上大部分产物中 Adda 的共轭碳双键均被破坏, FA 溶液中及去离子水中 MC-LR 的光解途径主要通过 Adda 基团的共轭双键断裂以及酰胺键的断裂实现的。

Results

Tab.1 Kinetic equations and parameters of photodegradation of MC-LR in FA solutions with different concentrations

FA 浓度 (mg L ⁻¹)	方程	一级动力学拟合		方程	二级动力学拟合	
		k ₁ /min ⁻¹	R ²		k ₂ /min ⁻¹	R ²
FA=2.5	ln(C ₀ /C)=0.00196t	0.00196	0.7335	1/C-1/C ₀ =0.00245t	0.00245	0.7765
FA=5	ln(C ₀ /C)=0.00259t	0.00259	0.9293	1/C-1/C ₀ =0.00290t	0.00290	0.9703
FA=7.5	ln(C ₀ /C)=0.00263t	0.00263	0.8734	1/C-1/C ₀ =0.00293t	0.00293	0.9821
FA=10	ln(C ₀ /C)=0.00179t	0.00179	0.9890	1/C-1/C ₀ =0.00227t	0.00227	0.9895
去离子水	ln(C ₀ /C)=0.00155t	0.00155	0.9269	1/C-1/C ₀ =0.00188t	0.00188	0.9336

Tab.2 Apparent rate constant and light shielding coefficient of MC-LR in FA solutions with different concentrations

FA 浓度 (mg L ⁻¹)	k _{obs(FA)}	S _λ	k _{obs(no-FA)}	S _λ	k _{FA}
FA=2.5	0.00245	0.611	0.0011		0.00135
FA=5	0.00290	0.542	0.0010		0.00190
FA=7.5	0.00293	0.489	0.0009		0.00203
FA=10	0.00227	0.442	0.0008		0.00147

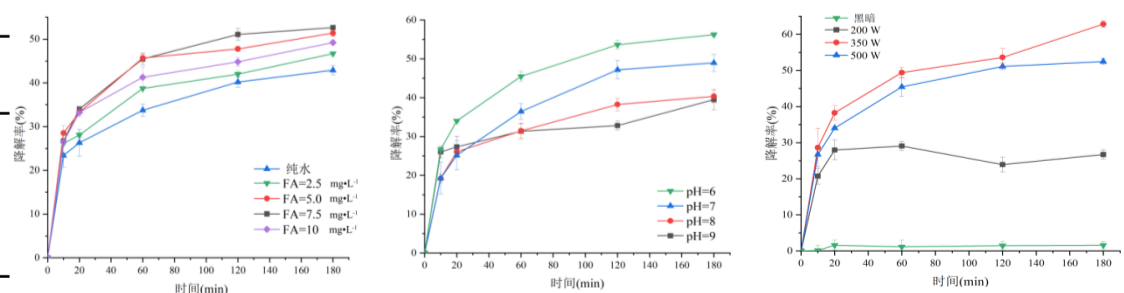


Fig.3 Photodegradation experiments of FA solutions with different concentrations and under different conditions

References

- Islam A et al. Transformation of microcystin-LR and olefinic compounds by ferrate(VI): Oxidative cleavage of olefinic double bonds as the primary reaction pathway[J]. Water Research, 2018.
- Wang H et al. Triplet photochemistry of dissolved black carbon and its effects on the photochemical formation of reactive oxygen species[J]. Environmental Science & Technology, 2020