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黄铁矿光化学氧化降解微囊藻毒素-LR 的机制

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摘要: 在可见光($\lambda > 420$ nm)照射和中性条件(pH=6.8)下, 采用天然黄铁矿降解微囊藻毒素 MC-LR, XRD 和 SEM 检测表明黄铁矿为层状结构, 反应前后黄铁矿表面 XPS 的表征说明矿物表面存在着 S 缺陷和缺陷位点 Fe(II) 到 Fe(III) 的转化过程。ESR 检测显示黄铁矿光化学反应体系涉及·OH 机制。HPLC 和 LC-MS 结果显示可见光照射能有效活化黄铁矿降解 MC-LR, 反应 10 h 时能完全降解 MC-LR, 20 h 时对 MC-LR 矿化率达到约 60%, 据实验结果推测出黄铁矿光化学氧化 MC-LR 的两条反应途径。

关键词: 黄铁矿; 光化学降解; 可见光; 微囊藻毒素-LR(MC-LR)

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Mechanism of Photochemical Degradation of MC-LR by Pyrite

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Abstract: Pyrite was used as catalyst to degrade Microcystin-LR (MC-LR) at pH 6.8 under visible light irradiation ($\lambda > 420$ nm). X-ray diffraction (XRD) and scanning electron microscope (SEM) characterization showed that pyrite had the layered structure. The ion state of pyrite before and after the reaction was identified using X-Ray Photoelectron Spectroscopy (XPS), confirming the conversion process of Fe(II) to Fe(III) on the sulfur defect sites. Electron Spin Resonance (ESR) test showed that pyrite photochemical reaction produced hydroxyl radical (·OH). The results of high performance liquid chromatography (HPLC) and liquid chromatograph-mass spectrometer (LC-MS) showed that visible light irradiation could effectively activate pyrite to degrade MC-LR. The degradation rate of MC-LR reached 100% after 10 hours and the mineralization rate reached 60% after 20 hours. The two reaction pathways of photochemical oxidation of MC-LR by pyrite were discussed.

Key words: pyrite; photochemical degradation; visible light; MC-LR

日益严重水体富营养化导致了世界范围内藻华频繁暴发^[1], 而由蓝藻水华产生的藻毒素会直接威胁水生动物和人类的生存及健康, 微囊藻毒素-LR (microcystins, MC-LR) 是其中分布最广毒性最强的一种藻毒素^[2,3]。高级氧化技术^[4] (advanced oxidation processes, AOPs) 是最有效降解 MC-LR 技术之一, 如研究发现 Fenton 技术^[5]、光催化纳米技术^[6]、氯和高锰酸盐氧化技术^[7]、臭氧^[8]和过硫酸盐氧化技术^[9]等多种 AOPs 技术^[10,11]均能有效降解 MC-LR。其中 Fenton 技术因其无选择性、反应迅速、处理彻底等优点, 成为最有前景的原位修复技术之一^[12]。

自然界中铁矿物由 Fe(III) 和 Fe(II) 等金属复合物组成, 是一个“天然”的类 Fenton 试剂, 研究其催化降解有机污染物可以有效探讨“自然原位”光催化机制^[13~17]。黄铁矿大量存在于自然

界中并在还原环境下有很好的稳定性, 是沉积物铁硫循环过程中的关键物质^[18,19]。目前对黄铁矿氧化的研究不仅仅只是涉及地质领域, 在化学领域中也广泛存在。Cohn 等^[20,21]研究了黄铁矿在水溶液中通过产生 H₂O₂ 转化成·OH, 从而对生命物质核酸等造成影响。Schoonen 等^[22]研究了黄铁矿在较大的 pH 范围内均能与分子氧作用发生氧化反应; Wang 等^[23]选择乳酸盐为模型目标得到黄铁矿对有机物具有良好催化氧化效率。Borda 等^[24]通过 XPS 的表征对比了反应前后黄铁矿表面的状态, 发现在黄铁矿表面确实由于存在 Fe(III) 和 Fe(II) 的相互转换过程而产生自由

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基;因此,黄铁矿通过产生活性物种 $\cdot\text{OH}$ 能应用于 MC-LR 的降解。

本文采用黄铁矿作为异相 Fenton 介质,在可见光照射下研究了其对藻毒素 MC-LR 的降解过程,发现反应 10 h 后,降解率达到了 100%,反应 20 h 矿化率达到约 60%。利用 XPS 跟踪降解前后黄铁矿表面元素的价态变化及氧化物种类的测定,确认黄铁矿光化学氧化反应体系确实产生 $\cdot\text{OH}$,结合 LC-MS 结果推测出黄铁矿光化学氧化 MC-LR 的两条反应途径。

1 材料与方法

1.1 试剂与仪器

主要实验试剂:黄铁矿(由中南冶金地质研究所提供的天然矿石);微囊藻毒素-LR (MC-LR)标准样品(每瓶 1 mg, $\geq 95\%$);购买于伊普瑞斯科技有限公司。实验所用其他试剂为分析纯,水为娃哈哈纯净水。

主要实验仪器:高效液相色谱仪(Waters2695, 美国);二维液相色谱-离子阱质谱联用仪(AmazonSL、1200 Agilent);XPA 系列光化学反应仪(南京胥江机电厂)。

1.2 实验过程

黄铁矿前处理:将黄铁矿进行碾磨后过 200 目筛得到实验所需要粒径大小的矿物粉末,密封保存。

样品表征:通过 X 射线衍射仪进行 XRD 分析主要组成,扫描电子显微镜(SEM)观察其形貌,X-射线光电子能谱仪进行 X 射线光电子能谱(XPS)的分析。

可见光光化学氧化降解 MC-LR:在 15 mL 圆柱形硬质玻璃管中加入 5 mL $2.0 \text{ mg}\cdot\text{L}^{-1}$ MC-LR 水溶液,然后加入黄铁矿粉末(终浓度为 $250 \text{ mg}\cdot\text{L}^{-1}$)置于暗室中搅拌 120 min 使其达到吸附平衡;再加光照射并开始计时,间隔一定时间取样 300 μL 。所有的反应均在 XPA 光反应器中进行,加光时使用截止型滤光片($\lambda > 420 \text{ nm}$)去除 420 nm 以下的光以保证反应仅在可见光下进行。

HPLC 分析:降解过程中不同时间点取样后进行离心并取上清液进行高效液相色谱。检测器为二极管阵列(Waters-PDA-2998, $\lambda = 238 \text{ nm}$),色谱条件为:KromasilC18 色谱柱(4.6 mm $\times$ 150 mm,粒径 10 μm),流动相为甲醇:水(含 0.05% 三氟乙酸) = 65:35, $v = 0.8 \text{ mL}\cdot\text{min}^{-1}$, $T = 40^\circ\text{C}$, $t_{\text{R(MC-LR)}} = 8.9 \text{ min}$ 。

2 结果与讨论

2.1 黄铁矿的 XRD、SEM 和 EDS 分析

黄铁矿的 XRD 图如图 1 所示,其主要成分为 FeS_2 ,属于等轴晶系,与卡号为 42-1340 的标准卡匹配,晶胞参数为: $a = b = c = 5.418$, $z = 4$ 。Fe 原子占据立方体晶胞的角顶和面心;S 原子组成对硫 $[\text{S}_2]^{2-}$,呈哑铃状,其中心位于晶胞棱的中心和体心。图 2(a)为黄铁矿的扫描电子显微镜(SEM)图片,可看出黄铁矿呈不规则层状结构。XRD 图谱上除 FeS_2 的特征峰外亦能看出含有少量的其他杂质,结合 EDS 元素表征[图 2(b)]可看出杂质成分主要为 CaO 、 SiO_2 、 Al_2O_3 等天然杂质。

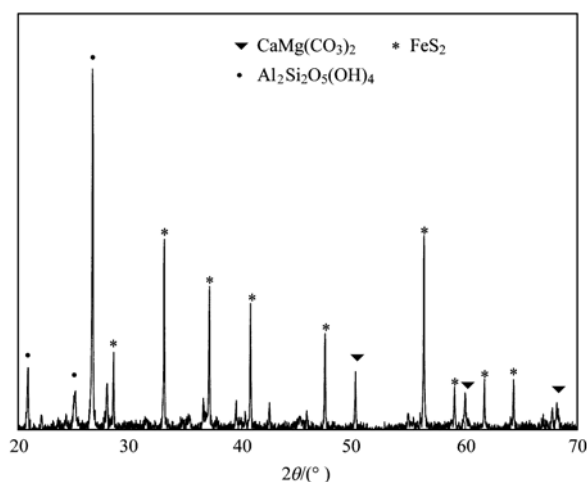


图1 黄铁矿的 XRD 图

Fig. 1 XRD pattern of pyrite

2.2 X 射线光电子能谱(XPS)分析

为了更深入地了解在藻毒素降解过程中黄铁矿所起到的作用,利用 XPS 对反应前后黄铁矿表面发生的变化进行了表征,结果如图 3 所示,其中 A、B 分别表示反应前后催化剂中 $\text{S}2p$ 和 $\text{Fe}2p$ 的 XPS 对比。如图 3 中所示,在长达 10 h 降解反应后,黄铁矿表面 FeS_2 的 $\text{S}2p$ (162.6 eV 和 169.5 eV) 整体蓝移至 163.9 eV 和 169.8 eV,这归属为 SO_4^{2-} 中 $\text{S}2p$ 电子结合能。同时 $\text{Fe}2p$ 电子结合能谱显示,反应前黄铁矿表面同时含有 FeS_2 (707 eV) 和 FeOOH (711.6 eV),反应后的 FeS_2 (707 eV) 峰消失,并在 712.3 eV [$\text{Fe}(\text{III})$] 产生一个新峰。表明反应过程中催化剂表面存在 $\text{S}^{2-} \rightarrow \text{SO}_4^{2-}$ 、 $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ 等氧化过程。结合 Cohn 等^[20] 和 Borda 等^[24] 的实验研究,进一步说明黄铁矿表面通过 $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ 不同价态间的转化与分子氧和水相互作用,使其转化产生 H_2O_2 和 $\cdot\text{OH}$ 进而与底物作用。可见光具有加速电子传递的作用。

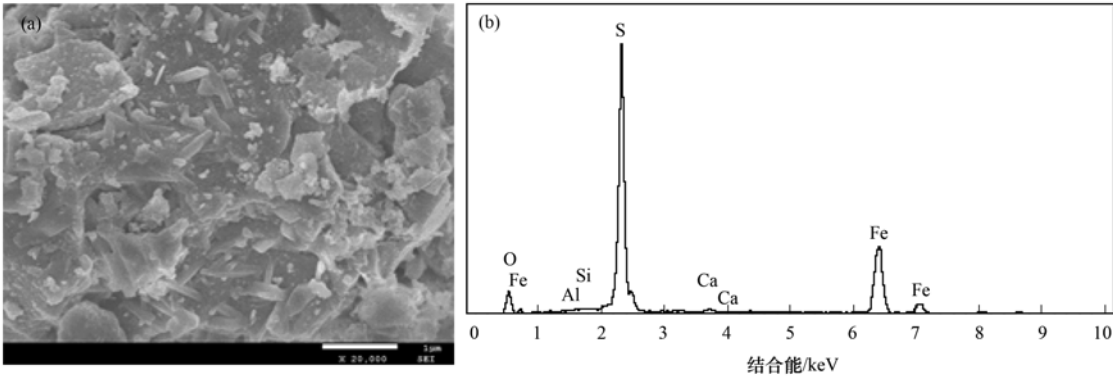


图 2 黄铁矿的 SEM 及 EDS 表征

Fig. 2 SEM images and EDS analysis of pyrite

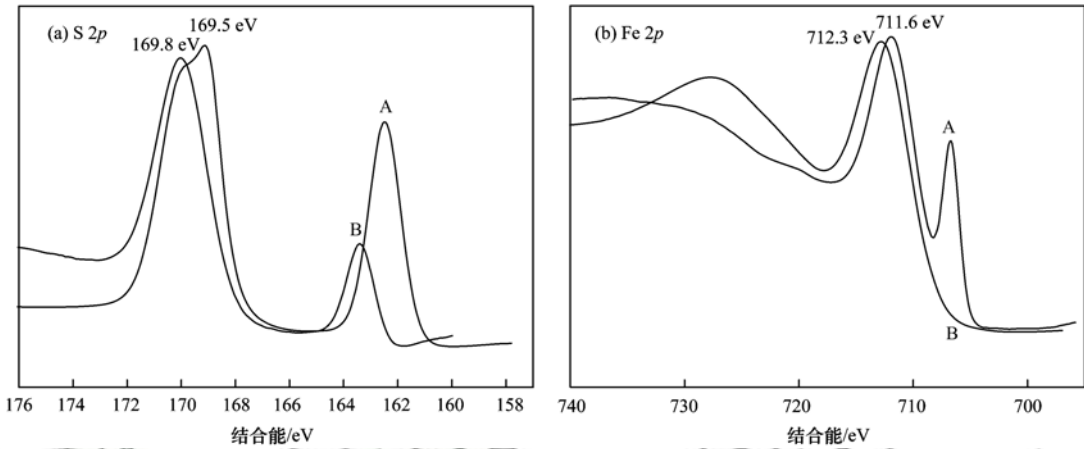


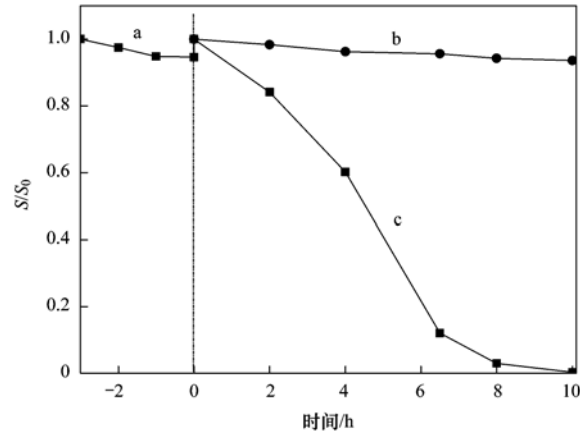
图 3 黄铁矿反应前后的 XPS 表征

Fig. 3 XPS patterns of pyrite before and after the reaction

2.3 在可见光条件下黄铁矿对 MC-LR 的降解和矿化在暗反应一段时间使其吸附达到平衡后加光,不同条件下 MC-LR 降解的动力学曲线如图 4. 从中可见,曲线 c 为 Vis/黄铁矿/MC-LR 体系的动力学曲线,显示出随着光化学反应的进行,MC-LR 浓度

逐渐降低,在反应时间 10 h 时,其降解率达到 100%. 而 Vis/MC-LR(曲线 a)体系中,MC-LR 的光解很少,几乎可以忽略,说明黄铁矿在可见光下能够有效地降解 MC-LR.

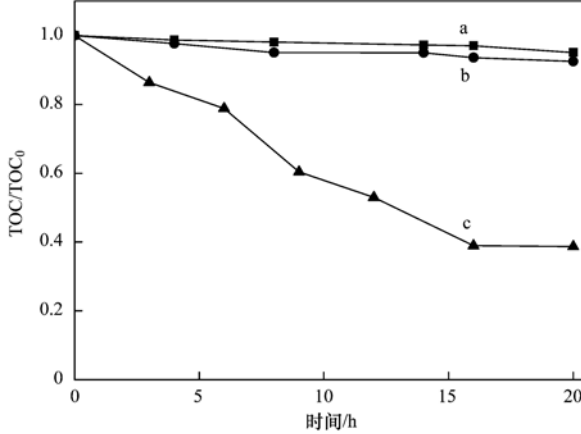
为了研究黄铁矿降解 MC-LR 过程中的氧化特



a. Vis/MC-LR; b. dark/pyrite/MC-LR; c. Vis/pyrite/MC-LR

图 4 黄铁矿降解 MC-LR 的动力学曲线

Fig. 4 Degradation kinetics curve of MC-LR on pyrite



a. Vis/MC-LR; b. dark/pyrite/MC-LR; c. Vis/pyrite/MC-LR

图 5 黄铁矿降解 MC-LR 过程中 TOC 的测定

Fig. 5 TOC measurements of pyrite catalytic degradation of MC-LR

性,本文分别对 Vis/MC-LR (曲线 a)、dark/黄铁矿/MC-LR (曲线 b)、Vis/黄铁矿/MC-LR (曲线 c) 这 3 个体系的降解过程进行了 TOC 的跟踪测定. 由图 5 可见,MC-LR 可见光光解较少,且在黄铁矿存在的暗反应条件下,MC-LR 也几乎不能矿化,而在黄铁矿存在的可见光体系反应 20 h 后,MC-LR 矿化率达到约 60%,表明在可见光照射下黄铁矿能有效

降解 MC-LR,且深度氧化 MC-LR 为二氧化碳、水以及一些其它的小分子化合物.

2.4 氧化物种分析测定

为了更深入地探究 Vis/黄铁矿/MC-LR 体系降解过程中产生的活性氧化物种和降解机制,笔者采用电子自旋共振技术检测来跟踪该反应过程中的瞬态自由基 $\cdot\text{OH}$ 的情况,结果见图 6. ESR 波谱中的强

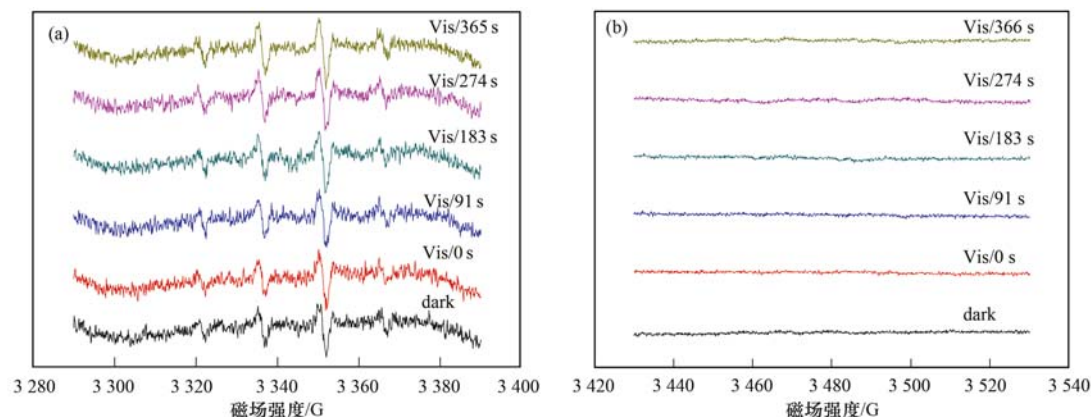


图 6 黄铁矿降解 MC-LR 过程中氧化物种的测定

Fig. 6 Measurement of oxidation species in the process of MC-LR degradation

度比为 1:2:2:1 四重峰特征峰即为 DMPO- $\cdot\text{OH}$ 加合物的特征信号峰 [图 6(a)],该体系在暗反应条件下有较弱的羟基信号,但可明显看出,在加光后信号明显加强,说明在光照下黄铁矿体系中能产生更强的 $\cdot\text{OH}$ 而更多更快地氧化底物. 而在反应过程中并未捕捉到超氧的信号峰 [图 6(b)],说明在该体系反应过程中,并未涉及超氧自由基的产生.

2.5 LC/MS/MS 对中间产物的结构鉴定

图 7 为 Vis/黄铁矿/MC-LR 体系降解过程不同时间点的总离子流. 随着反应的进行可以看到 MC-LR 浓度不断地减少直至完全消失,同时伴随着降解产物的生成. 通过提取底物 MC-LR (m/z 995.6) (见图 7) 和中间主要产物 m/z 1029.6、965.6 质谱图 (见图 8) 的 LC-MS 变化情况,可以看到,MC-LR 的峰逐渐降低,同时产生产物 m/z 1029.6 的四重峰,是 Adda 结构上共轭双键上的氧化产物,为 4 种可能的同分异构体^[25]. 另一种主要降解产物 m/z 965.6 含量逐渐累积而后再减少的现象,说明其被继续氧化降解.

2.6 MC-LR 光化学氧化机制

质荷比为 m/z 1009.6、 m/z 1011.6、 m/z 1029.6、 m/z 1045.5 等物质是在 Vis/黄铁矿/MC-LR 体系降解过程中质谱提取出的降解产物,据此推测了反应过程中黄铁矿表面产生的 $\cdot\text{OH}$ 对 MC-LR 的进攻位点,以及 2 条主要氧化降解途径 (图 9):

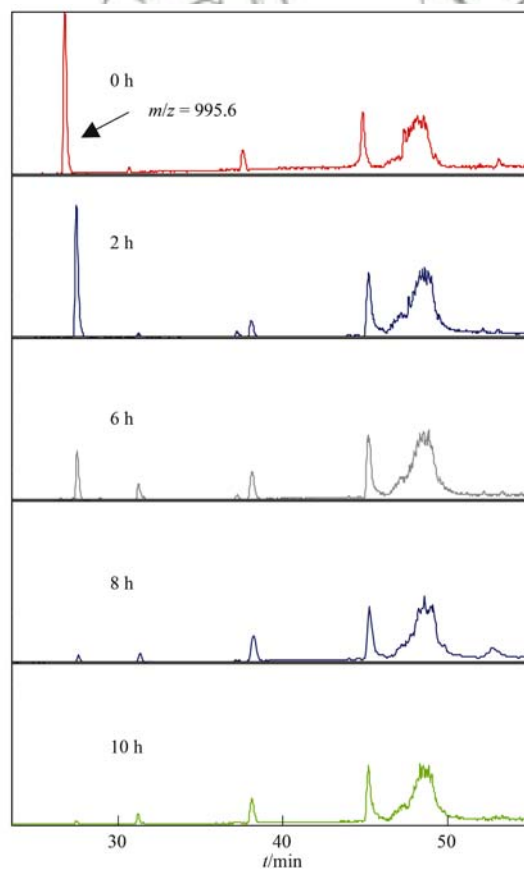


图 7 MC-LR 降解过程中各时间段的总离子流及 m/z 995.6 的变化

Fig. 7 Total ion chromatogram of MC-LR degradation at different reaction times and the changes in MC-LR m/z 995.6

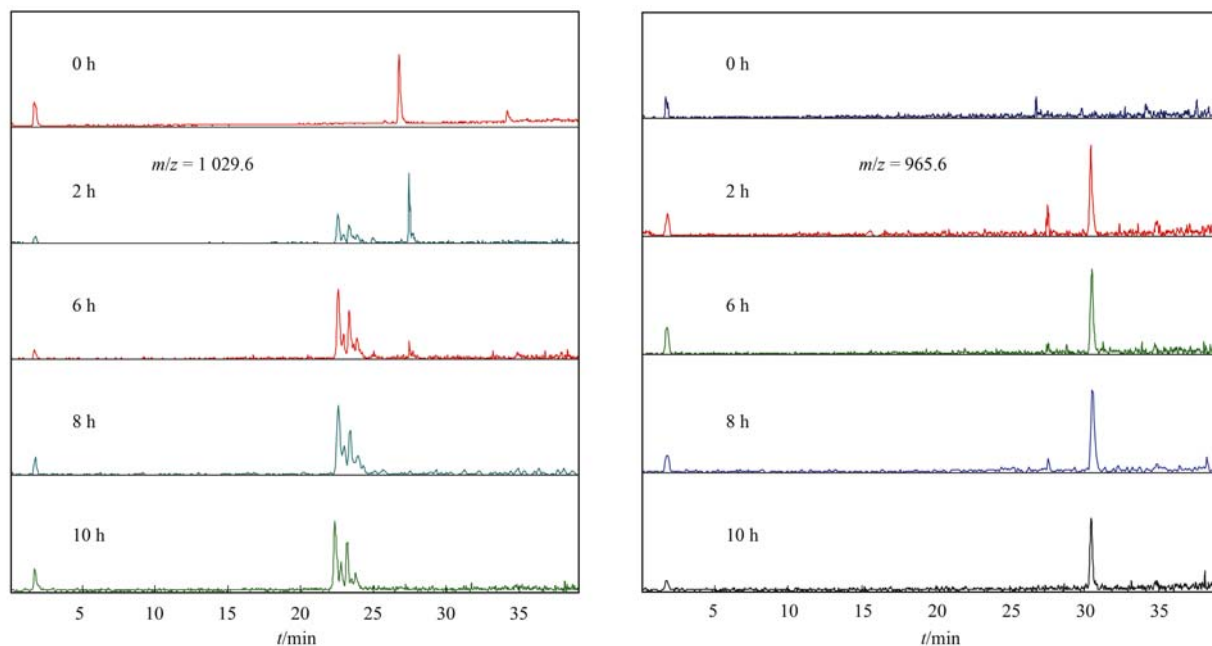


图 8 中间产物 m/z 1029.6, 965.6 的 LC-MS 变化

Fig. 8 Changes in the intermediate products m/z 1029.6, 965.6

①·OH容易进攻 Adda 链上的两个共轭双键(C4 与 C5、C6 与 C7)而发生羟基加成,由于—OH的位置不同,所以可产生 m/z 1029.6 的 4 种同分异构体,这与文献[26]报道一致.进而,Adda 链上苯环继续发生·OH取代形成产物 m/z 1045.5;② Adda 链的甲氧基被·OH氧化生成甲酸酯衍生物 m/z 1009,随后脱酯基得到产物 m/z 965.6.

3 结论

本文采用黄铁矿作为异相光化学介质,跟踪了 MC-LR 的降解过程及降解产物,讨论了黄铁矿在可见光光化学氧化降解 MC-LR 的机制;黄铁矿在可见光下可以有效地降解 MC-LR,反应 10 h 时能完全降解,20 h 时矿化率达到约 60%,且提出了 MC-LR 的光化学氧化降解机制主要涉及到·OH的高效氧化作用的两条降解途径.

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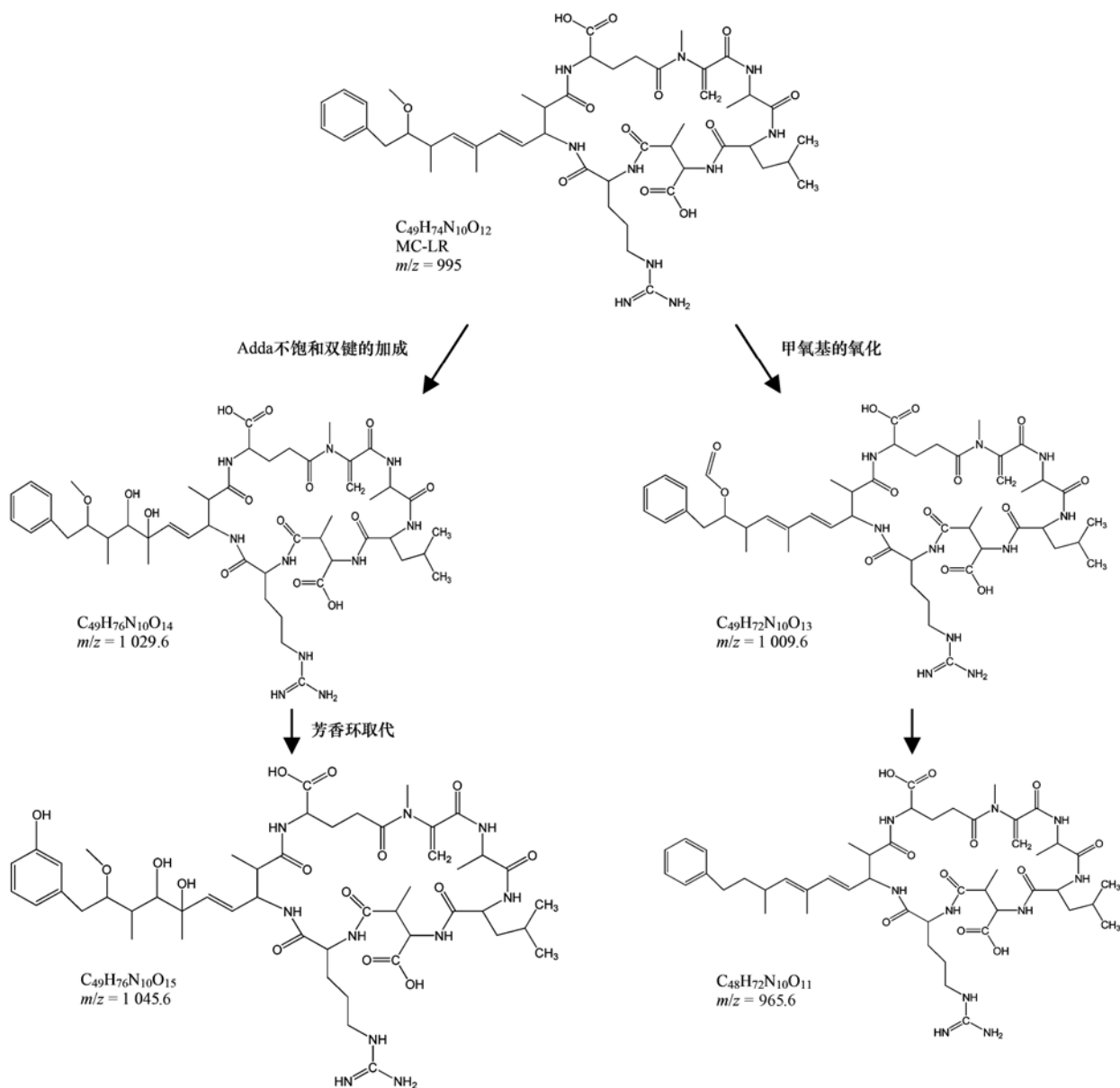


图9 黄铁矿光化学氧化降解 MC-LR 的主要初步氧化产物

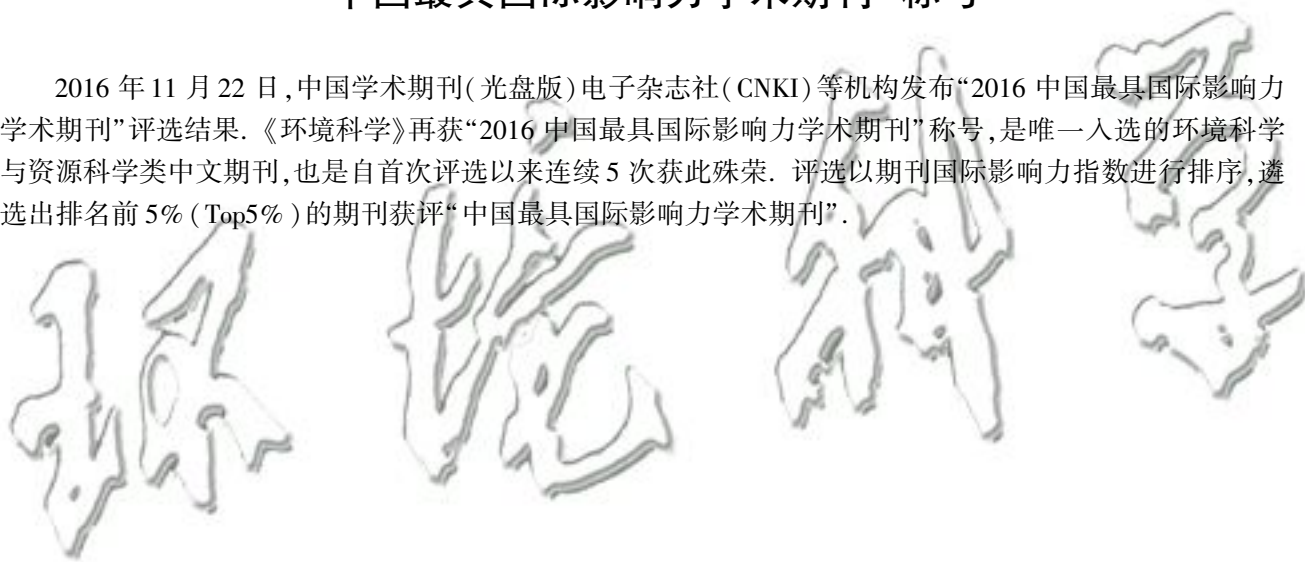
Fig. 9 Main intermediates in the photochemical degradation of MC-LR by Pyrite

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