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污泥生物炭活化过一硫酸盐降解环丙沙星

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摘要:以脱水干化污泥为原料,经450℃热解制成污泥生物炭(BC),活化过一硫酸盐(PMS),构建BC/PMS体系,降解环丙沙星(CIP).采用扫描电子显微镜(SEM)、X射线能谱(EDS)、傅里叶变换红外吸收光谱(FTIR)、X射线衍射(XRD)、Zeta电位分析仪和电子自旋共振(EPR)分析了BC的理化性质;考察了BC投加量、PMS投加量、初始pH值和无机阴离子对BC/PMS体系降解CIP效果的影响;通过自由基淬灭实验和X射线光电子能谱(XPS)分析,深入探讨了BC/PMS体系对CIP降解机制.结果表明,CIP降解率随BC投加量和PMS投加量增大而升高,随溶液初始pH增大而降低,在BC 1.0 g·L⁻¹、PMS 3.0 mmol·L⁻¹、初始pH 6.0、CIP 20 mg·L⁻¹和反应时间120 min时,CIP降解率为49.09%;SO₄²⁻和NO₃⁻对BC/PMS体系降解效果无显著影响,HCO₃⁻和Cl⁻具有明显抑制作用;BC/PMS体系降解CIP是自由基途径(·OH和SO₄·)和非自由基途径(¹O₂)共同作用的结果,降解路径主要包括哌嗪环开环和羟基化反应.

关键词:过一硫酸盐;污泥生物炭;环丙沙星;自由基;非自由基

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Degradation of Ciprofloxacin by Activating Peroxymonosulfate with Sludge Biochar

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Abstract: Sludge biochar (BC), which was prepared by the pyrolysis of waste-activated sludge at 450°C, was applied for peroxymonosulfate (PMS) activation to construct a BC/PMS system for ciprofloxacin (CIP) degradation. The physical and chemical properties of BC were studied using scanning electron microscopy (SEM), an energy dispersive spectrometer (EDS), a Fourier transform infrared spectrometer (FTIR), X-ray diffraction (XRD), a Zeta potential analyzer, and electron paramagnetic resonance spectroscopy (EPR). The effects of BC dosage, PMS dosage, initial pH value, and inorganic anions on CIP removal in the BC/PMS system were investigated. Further, the degradation mechanism of the BC/PMS system was speculated through the free radical quenching experiment and X-ray photoelectron spectroscopy (XPS) analysis. The results showed that the CIP degradation rate was 49.09% at a BC dosage of 1.0 g·L⁻¹, PMS of 3.0 mmol·L⁻¹, CIP of 20 mg·L⁻¹, and pH of 6.0 in 120 min. SO₄²⁻ and NO₃⁻ had no obvious effect on the removal of CIP in the BC/PMS system, whereas HCO₃⁻ and Cl⁻ could inhibit CIP degradation significantly. The CIP removal in the BC/PMS system was attributed to the common function of the radical pathway dominated by ·OH and SO₄· and the non-radical pathway dominated by ¹O₂. The CIP degradation pathway mainly included piperazine ring opening and hydroxylation reaction.

Key words: peroxymonosulfate (PMS); sludge biochar; ciprofloxacin; radical; non-radical

近年来,抗生素的过度使用对生态环境和人类健康已构成严重威胁^[1,2].作为喹诺酮类抗生素的典型代表,环丙沙星(CIP)具有结构复杂、残留时间长和污染范围广等特点,在水体中被频繁检出,引起广泛的社会关注^[3,4].

目前,CIP去除方法包括物理处理、生物处理和化学处理^[5].常见的物理吸附法处理周期长,实际应用较少^[2,6].尽管传统生物处理法操作简单且成本较低,但受抗生素废水的污染物浓度限制易出现污泥膨胀^[7,8].相比之下,基于过一硫酸盐(PMS)的高级氧化技术以氧化性强、适用范围广和环境友好等优势,逐渐成为解决水中抗生素污染的首选方式^[9,10].然而,PMS性能稳定且自分解速率较慢,导致单独添加PMS时污染物去除率偏低^[11,12].因此,需外加催化剂活化PMS,促进自由基产生,提高污染物降解效率.

污水厂大规模建设导致污泥产量逐年增加,污泥处理处置面临严峻挑战^[13~15].采用脱水干化污泥

制备生物炭,可以活化PMS去除污染物,并提供一种经济环保且可持续的污泥处理模式^[16].然而,生物炭对PMS活化机制尚未明确.

本文采用某污水厂脱水干化污泥制备生物炭(BC),考察BC/PMS体系对CIP降解效果,探究最优反应条件,通过自由基淬灭实验和活性位点等分析对降解机制进行深入探讨,并提出CIP可能降解路径,以期控制污染物排放及指导污水处理提供理论依据.

1 材料与方法

1.1 材料

过一硫酸氢钾、氢氧化钠、盐酸、甲醇、甲酸、乙腈、碳酸氢钠、氯化钠、盐酸、硫酸钠、硝酸钠、

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无水乙醇、叔丁醇和环丙沙星来自国药集团,若无特殊说明为分析纯.实验用水为去离子水.

1.2 生物炭制备

取适量脱水干化污泥(含水率40%)置于石英舟中,移入管式炉,持续通入氮气形成无氧环境.以恒定速率 $10^{\circ}\text{C}\cdot\text{min}^{-1}$ 加热至 450°C ,恒温热解120 min.随后,在氮气保护下冷却20 min,将制得BC研磨,过200目筛,在 60°C 烘箱中干燥6 h.

为排除BC对CIP吸附影响,设置BC单独吸附CIP实验,实验条件为:BC投加量 $1.0\text{ g}\cdot\text{L}^{-1}$ 、CIP质量浓度 $20\text{ mg}\cdot\text{L}^{-1}$ 、溶液初始pH 6.0以及反应时间120 min(结果见图2,CIP去除率为12.69%).待反应完成后,将BC从溶液中过滤并自然晾干,回收BC用于下一步实验操作.

1.3 实验方法

将装有200 mL CIP溶液的锥形瓶放入摇床中, 25°C 、 $200\text{ r}\cdot\text{min}^{-1}$ 恒温振荡.分别考察PMS投加量、BC投加量、初始pH值和无机阴离子对BC/PMS体系对CIP降解的影响.每隔一定时间用移液枪取样4 mL,并立即采用PTFE针式过滤器($0.22\text{ }\mu\text{m}$)过滤,加入1 mL甲醇溶液终止反应.同一组实验重复3次,取平均值.

在PMS投加量影响实验中,PMS投加量分别设定为0、0.25、0.5、1.0、2.0、3.0和 $4.0\text{ mmol}\cdot\text{L}^{-1}$,BC投加量为 $1.0\text{ g}\cdot\text{L}^{-1}$,溶液初始pH为6.0, $\rho(\text{CIP})$ 为 $20\text{ mg}\cdot\text{L}^{-1}$;在BC投加量影响实验中,BC投加量分别设定为0.2、0.4、0.8和 $1.0\text{ g}\cdot\text{L}^{-1}$,PMS投加量为 $3.0\text{ mmol}\cdot\text{L}^{-1}$,溶液初始pH为6.0, $\rho(\text{CIP})$ 为 $20\text{ mg}\cdot\text{L}^{-1}$;在溶液初始pH影响实验中,使用浓度为 $1.0\text{ mol}\cdot\text{L}^{-1}$ NaOH和 H_2SO_4 调节初始pH至设定值2.0、4.0、6.0、8.0和10.0,PMS投加量为 $3.0\text{ mmol}\cdot\text{L}^{-1}$,BC投加量为 $1.0\text{ g}\cdot\text{L}^{-1}$, $\rho(\text{CIP})$ 为 $20\text{ mg}\cdot\text{L}^{-1}$;在无机阴离子影响实验中,在催化反应前向CIP溶液中分别加入 NaNO_3 、 NaHCO_3 、 NaCl 和 Na_2SO_4 ,每种阴离子浓度为1、5和 $100\text{ mmol}\cdot\text{L}^{-1}$,以不添加无机阴离子实验组作为空白组.

采用甲醇(MeOH)作为硫酸根自由基($\text{SO}_4^{\cdot-}$)和羟基自由基($\cdot\text{OH}$)淬灭剂^[17],叔丁醇(TBA)作为 $\cdot\text{OH}$ 淬灭剂^[18],L-组氨酸作为单线态氧($^1\text{O}_2$)淬灭剂^[19].上述物质投加浓度分别为500、500和 $10\text{ mmol}\cdot\text{L}^{-1}$,定时取样并测定CIP质量浓度.

1.4 分析方法

采用扫描电子显微镜-X射线能谱仪(SEM-EDS, ZEISS Gemini 300, 德国)、傅里叶变换红外光谱仪(FTIR, TENSOR27, 布鲁克)、X射线衍射仪

(XRD, Rigaku SmartLab SE, 日本)、X射线光电子能谱仪(XPS, Thermo fisher Scientific, 美国)和Zeta电位分析仪(Malvern, 英国)测定消除吸附影响后的BC性质.采用电子自旋共振(EPR, Bruker, 德国)检测消除吸附影响后BC中持久性自由基.采用液相色谱仪(LC-20A, SHIMADZU, 日本)测定CIP质量浓度,分离色谱柱采用C18反相色谱柱($150\text{ mm}\times 4.6\text{ mm}$, $5\text{ }\mu\text{m}$),流动相为70%纯乙腈和含有0.1%甲酸溶液的超纯水,流速 $1.0\text{ mL}\cdot\text{min}^{-1}$,柱温 40°C ,进样体积 $10\text{ }\mu\text{L}$,检测波长277 nm.采用高效液相色谱-质谱法(HPLC-MS, Agilent 1100-Thermos TSQ Quantum Ultra, 美国)测定CIP降解中间产物.对CIP降解进行动力学拟合^[20],表观速率常数 k_{obs} 计算如下:

$$\ln(\rho_t/\rho_0) = -k_{\text{obs}}t \quad (1)$$

式中, t 为反应时间(min), ρ_t 和 ρ_0 分别为 t 时刻CIP质量浓度和CIP的初始质量浓度($\text{mg}\cdot\text{L}^{-1}$).

2 结果与讨论

2.1 BC表征

由图1(a)和图1(b)可知,BC具有不规则片状结构,且表面存在少量碎屑,这是由灰分中盐类分解重组和挥发性部分流失所致^[21,22].污泥炭化时,溢出大量气体,导致BC出现明显孔隙结构,拥有更多活性位点.EDS结果见图1(c),BC含有大量O元素,以有机和无机组分形式存在,有机组分主要包括羧基、羟基、醌类和酯基等表面含氧官能团,无机组分主要包括硫酸盐、碳酸盐和磷酸盐等^[23,24].此外,BC还含有Ca、Mg和Fe等金属元素,均来自污泥脱水时添加的调理剂.

FTIR分析结果见图1(d), 3428 cm^{-1} 处为较明显的—OH基团伸缩振动峰,可能来自C—OH键和 H_2O ^[25];高于 3600 cm^{-1} 处可能是游离—OH的伸缩振动峰^[26]; 2914 cm^{-1} 附近可能是C—H的伸缩振动峰; 1612 cm^{-1} 处可能是羰基、羧基和芳香环中C=O、—CONH—和C=C的伸缩振动峰^[27],以上官能团通常作为BC催化PMS降解污染物活性位点^[28].此外, 1423 cm^{-1} 附近的吸收峰与—CH₂和—CH₃键有关, 1033 cm^{-1} 处和 649 cm^{-1} 附近的吸收峰分别与C—O伸缩振动和金属氧化物有关^[29].

XRD结果见图1(e), 2θ 位于 20.86° 、 26.64° 、 50.14° 和 59.96° 尖锐峰分别代表 SiO_2 (100)、(101)、(112)和(211)晶面^[30,31]; 2θ 位于 23.02° 、 29.41° 、 35.97° 、 39.40° 和 48.51° 尖锐峰分别代表 CaCO_3 (012)、(104)、(110)、(113)和(116)晶面,

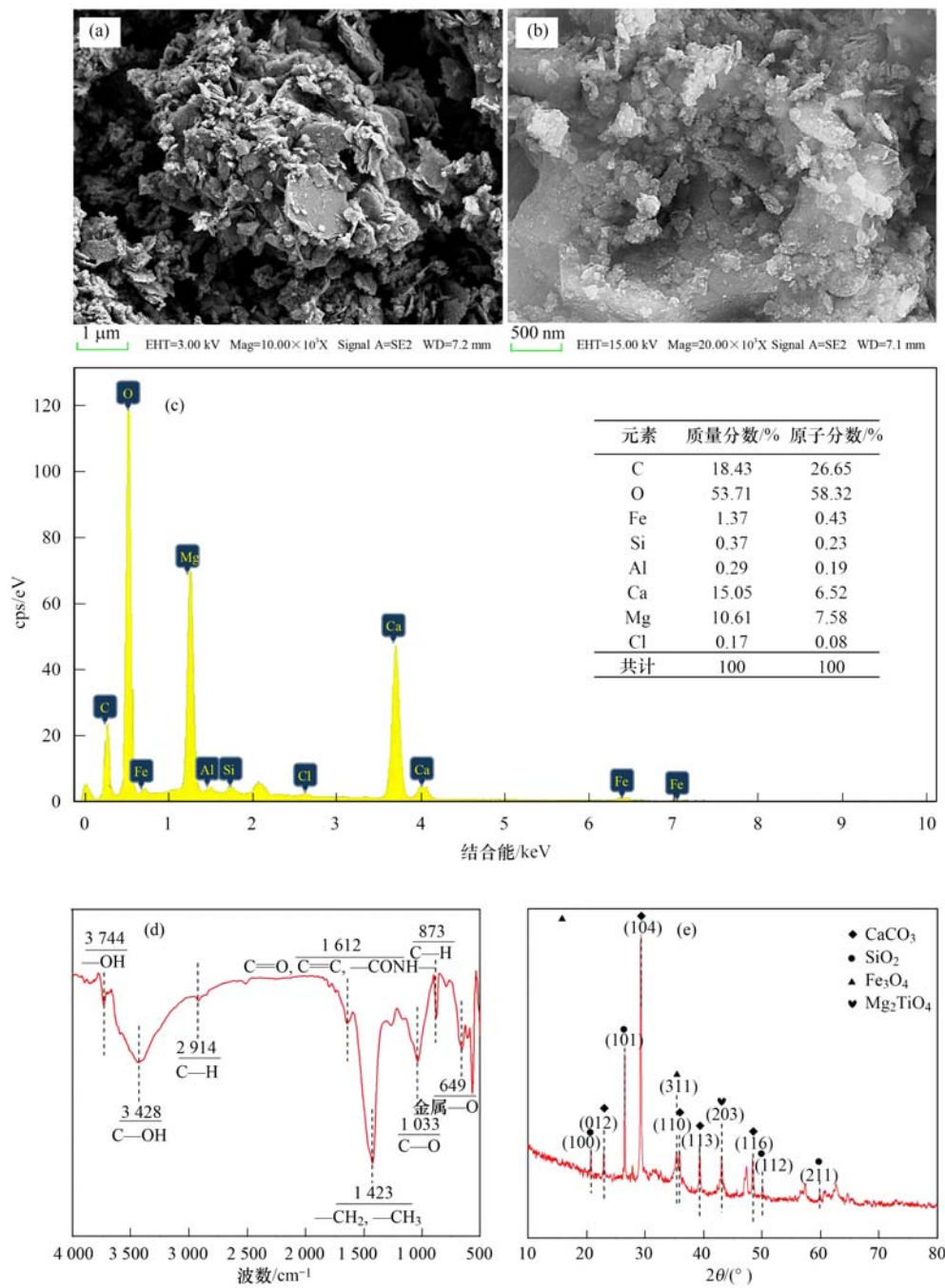


图 1 BC 的 SEM-EDS、FTIR 和 XRD 表征

Fig. 1 Characterization of BC through SEM-EDS, FTIR, and XRD

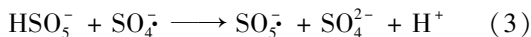
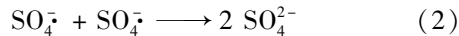
表明 SiO_2 和 CaCO_3 是 BC 主要结晶结构。

2.2 影响因素分析

2.2.1 PMS 投加量

由图 2 可见,仅投加 $3.0 \text{ mmol} \cdot \text{L}^{-1}$ PMS 时,CIP 质量浓度基本不变,说明未经催化的 PMS 无法直接氧化 CIP. 投加 PMS 和 $1.0 \text{ g} \cdot \text{L}^{-1}$ BC 时,CIP 质量浓度逐渐降低. PMS 投加量由 $0.1 \text{ mmol} \cdot \text{L}^{-1}$ 增至 $3.0 \text{ mmol} \cdot \text{L}^{-1}$,CIP 降解率与 k_{obs} 由 25.73% 和 0.0101 min^{-1} 升至 49.09% 和 0.0272 min^{-1} ,说明 PMS 经 BC 催化后加速降解 CIP. 当 PMS 投加量增至 $4.0 \text{ mmol} \cdot \text{L}^{-1}$ 时,CIP 降解率基本不变, k_{obs} 降至 0.0264

min^{-1} ,可能是过量 PMS 导致 $\text{SO}_4^{\cdot-}$ 自淬灭,生成不具有强氧化性的 SO_4^{2-} [式(2)]^[32]; 过量 PMS 与 $\text{SO}_4^{\cdot-}$ 和 $\cdot\text{OH}$ 反应生成氧化性更低的 $\text{SO}_5^{\cdot-}$ [式(3)~(4)],影响降解效果. 因此,最佳 PMS 投加量为 $3.0 \text{ mmol} \cdot \text{L}^{-1}$.



2.2.2 BC 投加量

由图 3 可见,当 BC 投加量为 $0.2 \text{ g} \cdot \text{L}^{-1}$ 时,催化剂活性位点不足导致 PMS 无法被有效活化,CIP

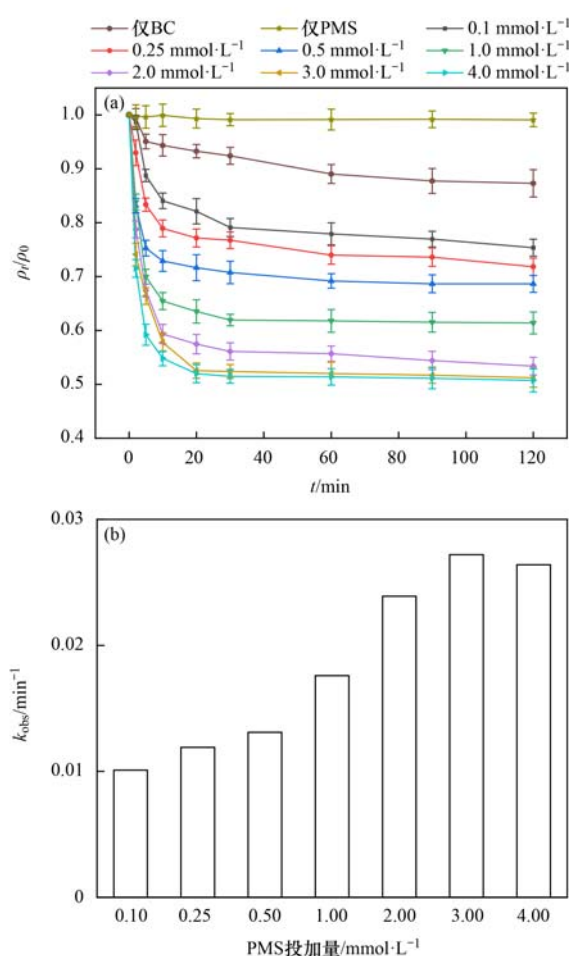


图2 PMS投加量对BC/PMS体系降解CIP的影响

Fig. 2 Effects of PMS dosage on CIP removal in BC/PMS

降解率仅为 11.95%, k_{obs} 仅为 $9.79 \times 10^{-4} \text{ min}^{-1}$. 当 BC 投加量逐渐增至 0.4、0.6、0.8 和 $1.0 \text{ g} \cdot \text{L}^{-1}$ 时, CIP 降解率分别升至 36.41%、41.96%、46.34% 和 49.09%, k_{obs} 分别升至 0.003 9、0.011 2、0.017 8 和 $0.027 2 \text{ min}^{-1}$. 这是因为高含量催化剂可提供更多活化 PMS 的表面活性位点, 提高污染物降解率^[33,34]. 因此, 最佳 BC 投加量为 $1.0 \text{ g} \cdot \text{L}^{-1}$.

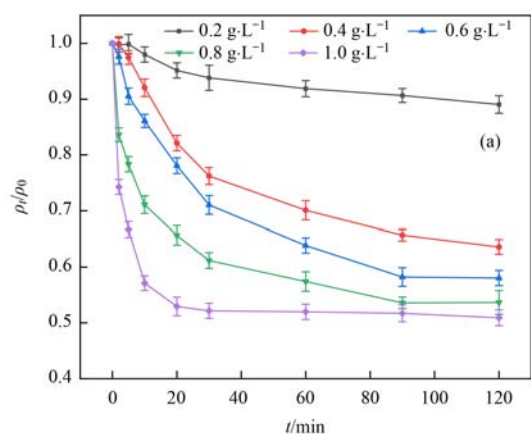


图3 BC投加量对BC/PMS体系降解CIP的影响

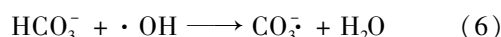
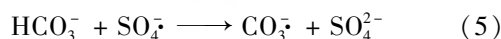
Fig. 3 Effects of BC dosage on CIP removal in BC/PMS

2.2.3 初始 pH

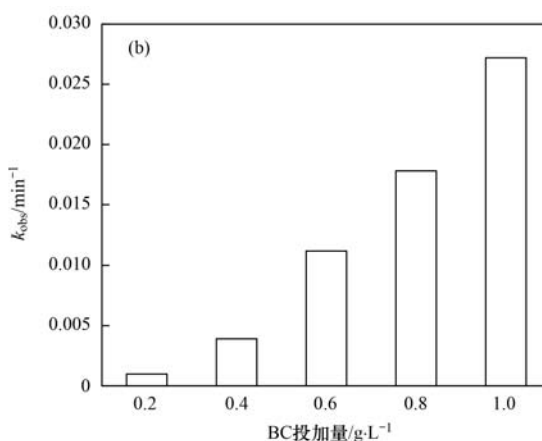
如图 4(a) 和图 4(b) 所示, 当 pH 值由 2.0 增至 10.0 时, CIP 降解率由 59.05% 降至 32.33%, k_{obs} 由 $0.056 5 \text{ min}^{-1}$ 降至 $0.011 4 \text{ min}^{-1}$, 这是由于初始 pH 直接影响 CIP (pK_{a} 为 6.2 和 8.8)^[8]、BC 和 PMS 的状态. 由图 4(c) 可见, $\text{pH} > 8.8$ 时 CIP 以 CIP^- 为主, $\text{pH} < 6.2$ 时以 CIP^+ 为主, $6.2 < \text{pH} < 8.8$ 时为 $\text{CIP}^{\pm}$. 由图 4(d) 可见, BC 零电荷点 pH_{pzc} 为 3.26, Zeta 电位随 pH 增加由正变负. 在酸性条件下, 尽管 BC 与 CIP 间存在静电斥力, 但溶液中 $\text{SO}_4^{\cdot-}$ 浓度较高, 促进 CIP 降解; 在碱性条件下, PMS 自我分解生成氧化能力较弱的 $\text{SO}_5^{\cdot-}$, 同时 $\text{SO}_4^{\cdot-}$ 与 OH^- 生成氧化能力较弱的 $\cdot\text{OH}$ ^[35], 减缓 CIP 降解. 实际污水 pH 值通常为 6.0 ~ 8.0, 考虑实用性, BC/PMS 体系溶液初始 pH 值调至 6.0.

2.2.4 无机阴离子

由图 5(a) 和图 5(b) 可见, 投加 1、5 和 $100 \text{ mmol} \cdot \text{L}^{-1}$ SO_4^{2-} 或 NO_3^- , CIP 降解率基本不变, 说明它们对 BC/PMS 体系的影响可以忽略. 投加 HCO_3^- 后, CIP 降解率降低, 由图 5(c) 可见, HCO_3^- 浓度由 $1 \text{ mmol} \cdot \text{L}^{-1}$ 增至 $100 \text{ mmol} \cdot \text{L}^{-1}$ 时, CIP 降解率由 48.78% 降至 32.43%. 这可能是因为过量 HCO_3^- 与 $\text{SO}_4^{\cdot-}$ 和 $\cdot\text{OH}$ 反应生成氧化能力较弱的 $\text{CO}_3^{\cdot-}$ ^[36,37], 影响 CIP 降解 [式(5)和式(6)].



由图 5(d) 可见, 当 Cl^- 浓度为 $1 \text{ mmol} \cdot \text{L}^{-1}$ 时, CIP 降解率降至 46.34%; 当 Cl^- 浓度增至 $5 \text{ mmol} \cdot \text{L}^{-1}$ 和 $100 \text{ mmol} \cdot \text{L}^{-1}$ 时, CIP 降解率降至 39.37% 和 35.47%. 这是因为 Cl^- 与 $\text{SO}_4^{\cdot-}$ 和 $\cdot\text{OH}$ 反应, 生成氧化能力较弱的 $\text{Cl} \cdot$ 和 $\text{ClOH} \cdot$ ^[19], 见式(7)和式(8). 当 Cl^- 浓度继续增加时, CIP 降解率下



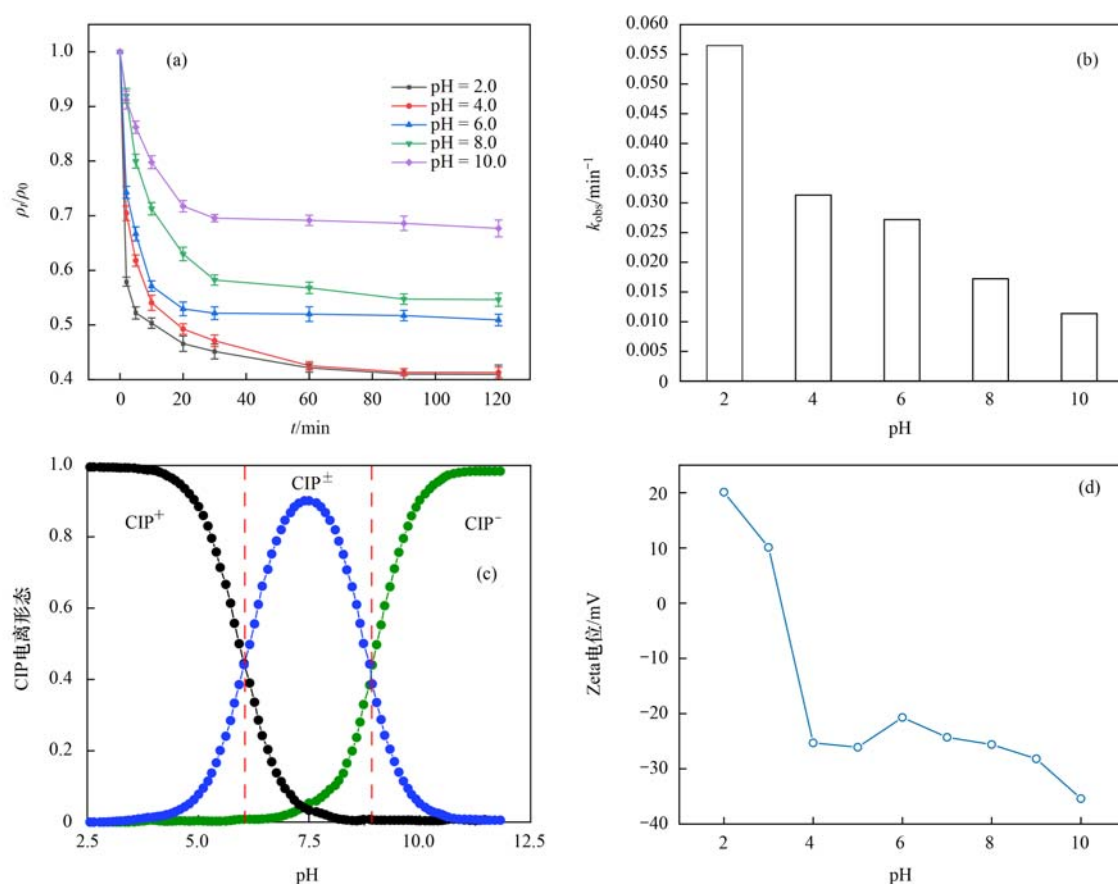
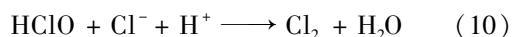
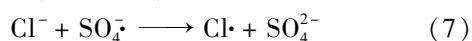


图4 溶液初始 pH 对 BC/PMS 体系降解 CIP 的影响

Fig. 4 Effects of the initial pH on CIP removal in BC/PMS

降幅度较小,这可能是因为 Cl^- 直接与溶液中 PMS 反应生成 HClO , 形成氧化性较强的 Cl_2 , 氧化降解 CIP^[38], 见式(9)和式(10)。



2.3 BC/PMS 体系降解 CIP 机制研究

2.3.1 活性物质鉴定

如图6所示,投加 $500 \text{ mmol} \cdot \text{L}^{-1}$ TBA 时, CIP 降解率由 49.09% 降至 38.77%, k_{obs} 由 0.0272 min^{-1} 降至 0.0161 min^{-1} ; 投加 $500 \text{ mmol} \cdot \text{L}^{-1}$ MeOH 时, CIP 降解率降至 32.23%, k_{obs} 降至 0.0131 min^{-1} , 说明 BC/PMS 体系同时生成 $\cdot\text{OH}$ 和 $\text{SO}_4^{\cdot-}$, 贡献率分别为 40.6% 和 11.1%, 见式(11)和式(12)。因此, $\cdot\text{OH}$ 是主要活性物质。

$$\cdot\text{OH} \text{ 贡献率} = (k_{\text{control}} - k_{\text{TBA}})/k_{\text{control}} \quad (11)$$

$$\text{SO}_4^{\cdot-} \text{ 贡献率} = (k_{\text{TBA}} - k_{\text{MeOH}})/k_{\text{control}} \quad (12)$$

在以生物炭为催化剂活化 PMS 降解污染物体系中, 还存在以 $^1\text{O}_2$ 为主的非自由基催化途径^[39,40]。由图6可见, 投加 $10 \text{ mmol} \cdot \text{L}^{-1}$ L-组氨酸后, CIP 降解受到明显抑制, 120 min 内降解率仅为 18.37%, 说

明 $^1\text{O}_2$ 在 BC/PMS 体系降解 CIP 中发挥作用。

2.3.2 表面活性位点及持久性自由基分析

采用 XPS 分析反应前后 BC 表面化学组成, 结果见图7。由图7(a)可见, 在 284.8 eV 处存在 C 1s 峰, 在 530.1 eV 处存在 O 1s 峰, 在 709.6 eV 处存在 Fe 2p 峰, 在 400 eV 附近出现 N 1s 峰。

C 1s 细分谱图见图7(b)。反应前 BC 存在 3 个特征峰, 分别对应石墨碳的 C—C 或 C=C (284.8 eV)、酚醇的 C—O (286.3 eV) 和羧基或酯基的 O=C—O (289.3 eV)。反应后 C—O 含量由 38.33% 降至 32.62%, O=C—O 含量由 24.47% 降至 11.09%, 证实酚、醇和羧基等官能团可能是 BC 中活性位点^[41]。

N 1s 细分谱图见图7(c)。反应前 BC 存在 2 个特征峰, 分别对应吡啶氮 (398.9 eV) 和吡咯氮 (400.4 eV); 反应后 BC 存在 3 个特征峰, 分别对应吡啶氮 (398.9 eV)、吡咯氮 (400.5 eV) 和硝酸盐氮 (405.2 eV)。同时, 吡啶氮含量由 42.37% 降至 23.38%, 吡咯氮含量由 57.62% 升至 68.58%, 说明吡啶氮是 BC 活化 PMS 降解 CIP 主要活性位点^[42,43]。

O 1s 细分谱图见图7(d)。反应前 BC 存在 3 个

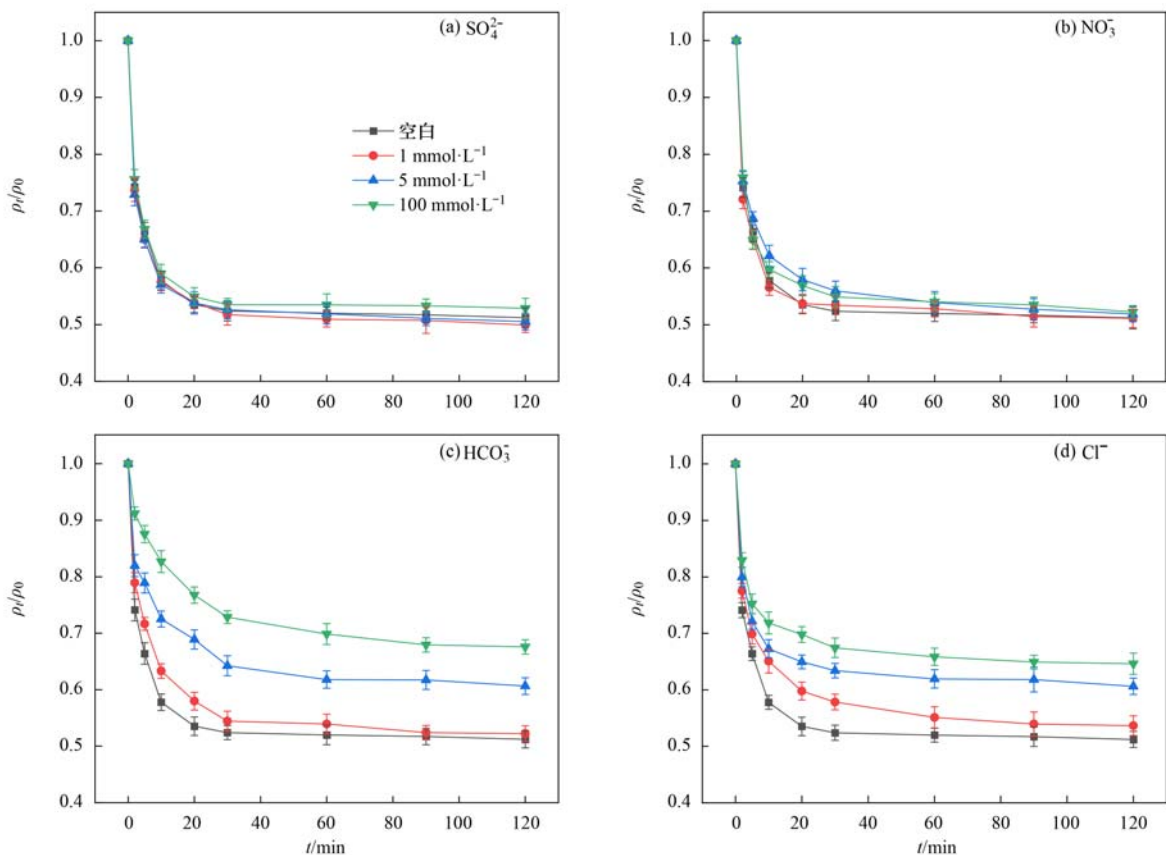


图5 常见阴离子(SO_4^{2-} 、 NO_3^- 、 HCO_3^- 和 Cl^-)对 BC/PMS 体系降解 CIP 的影响
Fig. 5 Effects of anions(SO_4^{2-} , NO_3^- , HCO_3^- , and Cl^-) on CIP removal in BC/PMS

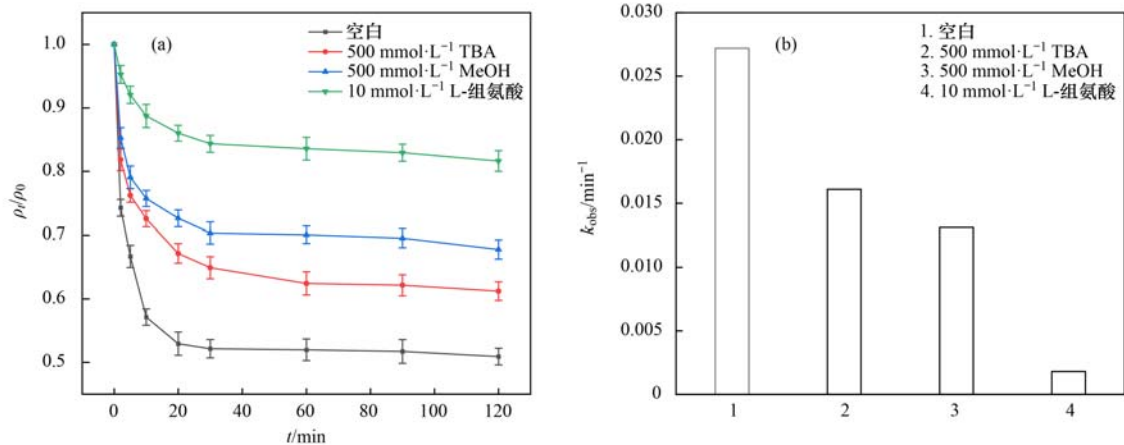


图6 BC/PMS 体系自由基淬灭实验

Fig. 6 Radical quenching experiment in BC/PMS

特征峰, 分别对应金属氧化物 (530.3 eV)、C—O (531.5 eV) 和 C=O (533.0 eV), 含量分别为 18.43%、64.40% 和 17.16%; 反应后酮类 C=O 和酚醇类 C—O 含量降低. 这可能是因为羰基 C=O 作为具有孤对电子的 Lewis 碱性位点, 有效增加相邻碳原子的电子密度, 进而活化 PMS^[44].

Fe 2p 细分谱图见图 7(e). 反应前 BC 的 Fe 2p 谱图在 709.7 eV、711.3 eV、723.3 eV 和 724.9 eV 处出现 4 个特征峰, 分别表示 $\text{Fe}^{2+} 2p_{3/2}$ 、 $\text{Fe}^{3+} 2p_{3/2}$ 、

$\text{Fe}^{2+} 2p_{1/2}$ 和 $\text{Fe}^{3+} 2p_{1/2}$, 反应后 4 个特征峰位置在 710.3 eV、711.9 eV、723.9 eV 和 725.5 eV. 反应后 BC 中 Fe^{2+} 的含量从 50.38% 下降至 34.79%, 表明 $\text{Fe}^{3+}/\text{Fe}^{2+}$ 氧化还原共轭对参与了 PMS 活化过程^[45].

此外, BC 含具有氧化还原能力的持久性自由基, 可转移电子活化 PMS^[25,28,46]. 由图 7(f) 可见, 持久性自由基浓度为 $15.91 \times 10^{15} \text{ spins} \cdot \text{g}^{-1}$, 是以氧原子为中心的半醌类自由基(g 因子 > 2.0040).

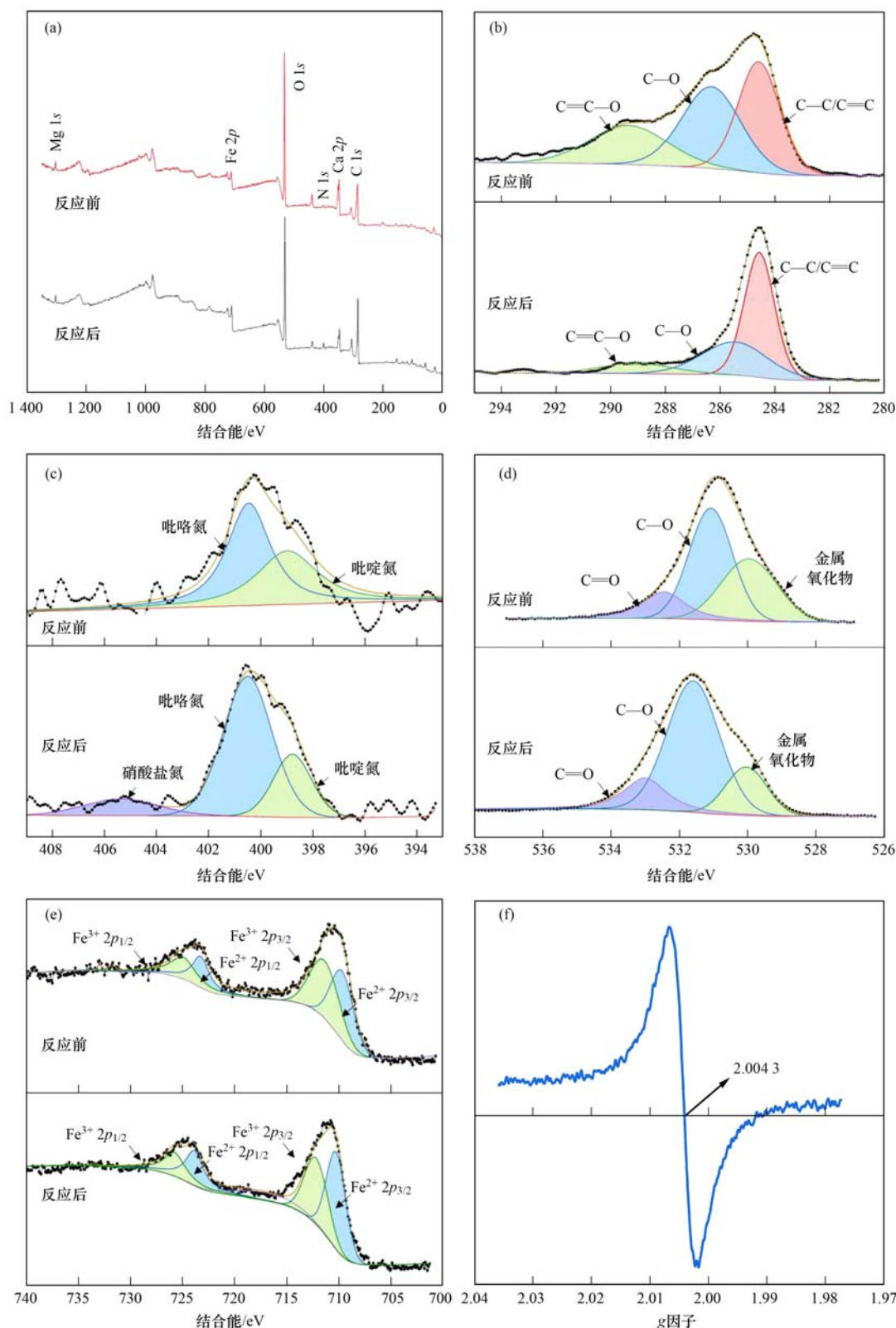


图7 BC反应前后XPS图谱和EPR图

Fig. 7 XPS spectra of the BC before and after the reaction and EPR spectra of BC

2.3.3 BC/PMS体系催化机制分析

BC活化PMS降解CIP机制见图8。BC/PMS体系同时存在自由基途径和非自由基途径。前者包括：BC中C=O、—OH和—COOH等含氧官能团及缺陷导致PMS中O—O断裂；BC中Fe³⁺/Fe²⁺氧化还

原共轭对参与PMS活化；吡啶氮具有孤对电子，促进自由流动的 π 电子从 sp^2 碳中转移到PMS，从而活化PMS；此外BC以氧原子为中心的半醌类自由基可转移电子活化PMS。后者包括：PMS形成 $SO_5^{\cdot-}$ 的自反应[式(13)和式(14)]；以氧原子为中心的

半醌类自由基活化氧分子生成超氧自由基及其进一步转化生成 $^1\text{O}_2$ ^[20];同时,BC具有一定的吸附能力,可以促进PMS和CIP接触,加速电子从CIP转移到PMS,从而促进 $^1\text{O}_2$ 的生成。

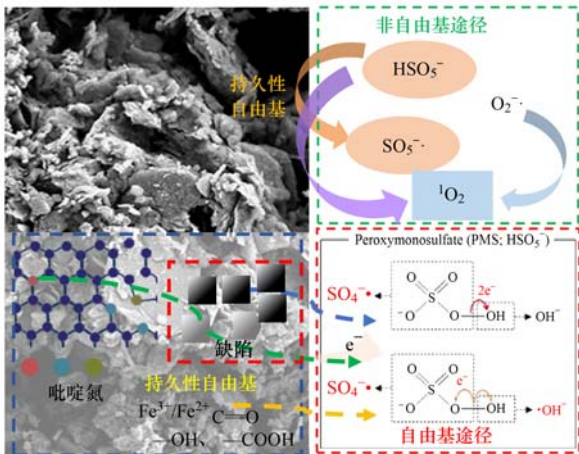
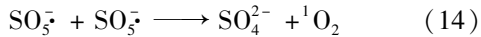
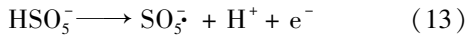


图8 BC/PMS体系催化机制

Fig. 8 Possible catalytic mechanism of BC/PMS system

2.4 BC/PMS体系降解路径分析

有研究表明,在亲电反应中,因电子易于在 $2\text{FED}_{\text{HOMO}}^2$ 值处获得,故在有较高 $2\text{FED}_{\text{HOMO}}^2 + \text{FED}_{\text{LUMO}}^2$ 值的位置容易受到自由基攻击^[47].基于HPLC-MS结果,推测CIP降解路径主要包括哌嗪环开环和羟基化反应,见图9。

途径1为CIP哌嗪环开环,有研究表明,CIP中哌嗪环是最容易受到自由基攻击的部位,其侧环被 $\text{SO}_4^{\cdot-}$ 、 $\cdot\text{OH}$ 及 $^1\text{O}_2$ 等氧化活性物质攻击后氧化分解^[4].CIP哌嗪侧环开环后产生P1($m/z = 334$),通过甲醛损失生成P2($m/z = 306$),并通过 CH_3N 基团损失以及氧化和脱碳产生P3($m/z = 291$).P3进一步氧化生成P4($m/z = 263$),从而使得CIP中哌嗪环被完全打开.P4经过脱氟作用和氧化作用,生成中间产物P5($m/z = 208$)、P6($m/z = 100$)和P7($m/z = 88$).途径2为羟基化反应,CIP经羟基化作用转化为P8($m/z = 330$),P8进一步被 $\text{SO}_4^{\cdot-}$ 、 $\cdot\text{OH}$ 及 $^1\text{O}_2$ 等攻击生成P7($m/z = 88$).最后,BC/PMS体系生成的中间产物可能被矿化为 CO_2 和 H_2O ,或是进一步

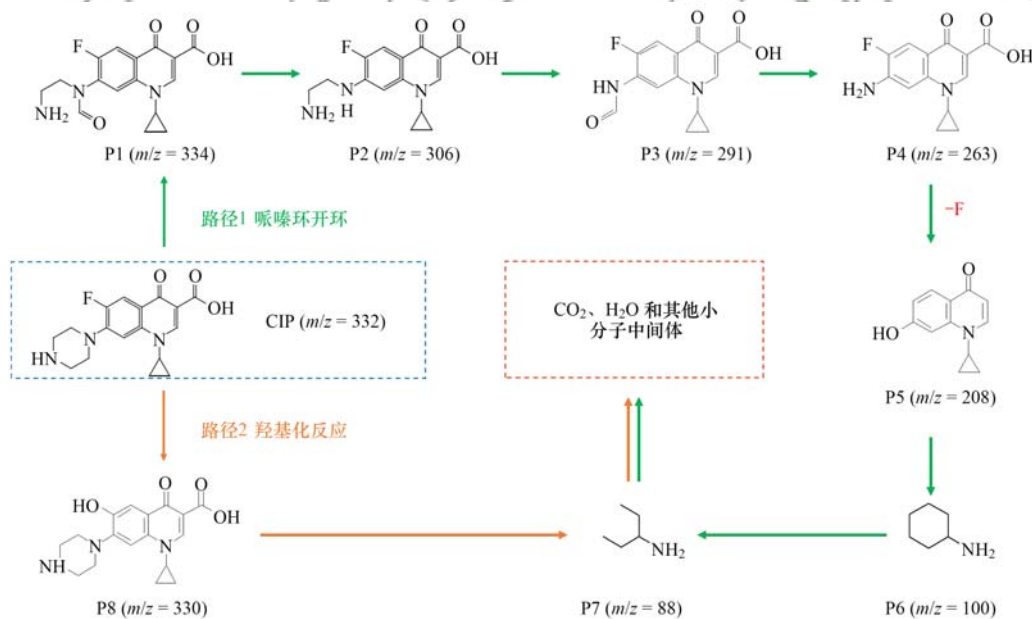


图9 BC/PMS体系中CIP降解路径

Fig. 9 Possible degradation pathways of CIP in the BC/PMS system

降解转化为其他小分子有机物.有研究表明,CIP毒性主要与结构中哌嗪环和氟有关,当哌嗪环开环及脱氟后,其毒性明显降低^[2].

3 结论

(1)BC具有形状不规则的片状结构,表面存在少量碎屑,含有大量氧元素及少量金属元素、丰富的含氧官能团及脂肪结构官能团, SiO_2 和 CaCO_3 为主要结晶结构。

(2)BC/PMS体系中CIP降解率随BC投加量、PMS投加量增大而升高,随溶液初始pH增大而降低.当BC投加量 $1.0 \text{ g} \cdot \text{L}^{-1}$ 、PMS投加量 $3.0 \text{ mmol} \cdot \text{L}^{-1}$ 和初始pH为6.0时,BC/PMS体系降解效果最佳,在120 min内 $20 \text{ mg} \cdot \text{L}^{-1}$ CIP降解率达到49.09%, k_{obs} 为 0.0272 min^{-1} . SO_4^{2-} 和 NO_3^- 对BC/PMS体系降解效果无显著影响,而 HCO_3^- 和 Cl^- 具有明显抑制作用。

(3)BC/PMS体系中自由基($\cdot\text{OH}$ 与 $\text{SO}_4^{\cdot-}$)和非

自由基($^1\text{O}_2$)共同参与 CIP 降解,其中 $\cdot\text{OH}$ 与 $\text{SO}_4\cdot^-$ 的贡献率分别为 40.6% 和 11.1%; CIP 降解路径主要包括哌嗪环开环和羟基化反应。

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Microbial Diversity and Population Structure of Different Salinized Soil Types in Hebei Province	LIU Yin-shuang, NIU Hong-jin, ZHAO Yang-yang, <i>et al.</i>	(7004)
Functional Genomics Analysis of Nitrogen and Phosphorus Transformation in Maize Rhizosphere Microorganisms	WANG Xiang-jun, JIANG Mei-tong, LI Sen, <i>et al.</i>	(7014)
Remediation of Soil Cadmium Contamination by <i>Solanum nigrum</i> L. Enhanced by the Combination of Exogenous Bacteria and Citric Acid	WANG Kai, WANG Li, WANG Yi-kun, <i>et al.</i>	(7024)
Effect of Combined Application of an <i>Enterobacter</i> and Sulfur Fertilizer on Cadmium and Arsenic Accumulation in Rice	ZHANG Pu-xin, YAO Jun-fan, LIU Yu-ling, <i>et al.</i>	(7036)