Sulfadiazine Degradation via Peroxydisulfate Activation: Insights into Boron and Sulfur Co-Doped Biochar and the Role of Singlet Oxygen

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Texts

Text S1 Chemicals

Boric acid (H_3BO_3, AR), thiourea (CH_3N_2S, AR), potassium persulfate ($K_2S_2O_8$, AR), sulfadiazine (SDZ, $C_{10}H_{10}N_4O_2S$, 98%), methanol (CH_3OH, HPLC), tert-butanol ($C_4H_{10}O$, AR), furfuryl alcohol ($C_5H_6O_2$, AR), p-benzoquinone ($C_6H_4O_2$, AR), hydrochloric acid (HCl, 36%~38%), sodium hydroxide (NaOH, AR), sodium chloride (NaCl, AR), sodium dihydrogen phosphate (NaH_2PO_4, AR), sodium bicarbonate ($NaHCO_3$, AR), humic acid (HA, AR), methyl orange (MO, $C_{14}H_{14}N_3NaO_3S$, Ind), rhodamine B (RhB, $C_{28}H_{31}ClN_2O_3$, AR), oxytetracycline (OTC, $C_{22}H_{24}N_2O_9$, >98%), bisphenol A (BPA, $C_{15}H_{16}O_2$, >99.5%), and phenol (C_6H_6O, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Absolute ethanol (C_2H_6O, AR) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd., China.

Text S2 Calculation of XRD-related parameters

The average interlayer spacing (d_{002}) of graphene-like nanosheets in the biochar samples was estimated based on Bragg's equation, where λ is the X-ray wavelength (0.154 nm) and θ_{002} represents the diffraction angle corresponding to the (002) reflection.

$$d = \frac{\lambda}{2sin\theta_{002}}$$

Text S3 Tests of organic pollutants

Organic pollutants were quantified using UV–visible spectrophotometry at specific wavelengths: 463 nm for methyl orange (MO), 544 nm for rhodamine B (RhB), and 270 nm for phenol. Sulfadiazine (SDZ), oxytetracycline (OTC), and bisphenol A (BPA) were analyzed by ultra-performance liquid chromatography coupled with UPLC–MS under the following conditions:

Compound	Mobile Phase	Ionization Mode	Precursor Ion (m/z)	Product Ions (m/z)
SDZ	Acetonitrile : 0.1% formic acid in water	ESI+	251.1	**156**/108
OTC	Acetonitrile : 0.1% formic acid in water	ESI+	461.4	443/**426**
BPA	Methanol : water	ESI-	227.1	211/**133**

Text S4 pH_{pzc}

The point of zero charge (pH_{pzc}) of the catalyst was determined using the pH drift method. Briefly, 50 mL of 0.1 M $NaNO_3$ solution was adjusted to initial pH values of 3, 5, 7, 9, and 11 using 0.1 M HCl or NaOH. The solutions were purged with N_2 for 10 min to remove dissolved CO_2, followed by the addition of 50 mg of biochar to each flask. The sealed suspensions were then shaken in a thermostatic incubator at 25 °C and 150 rpm for 24 h to reach equilibrium. Final pH values (pH_f) were recorded and plotted against the initial pH (pH_i). The point at which the ΔpH (pH_i – pH_f) crossed zero was identified as the pH_{PZC}.

Text S5 The Water Parameters of Different Water Matrices

	Tap Water	Lake Water
Temperature	18~20℃	15~18 ℃
pH	8.01~8.32	7.35~7.90
TOC	2.28~2.92 mg·L^{-1}	7.32~9.20 mg·L^{-1}
COD_{Mn}	1.28~1.72 mg·L^{-1}	3.75~4.90 mg·L^{-1}
TDS	189.2~207.7 mg·L^{-1}	302.1~376.4 mg·L^{-1}

Text S6 Estimation of Reactive Species Contributions

The relative contributions of different reactive species involved in SDZ degradation were estimated based on the kinetic suppression induced by specific scavengers, following a method reported in previous studies[1]. The apparent pseudo-first-order rate constants were calculated from the initial stage of the reaction under different quenching conditions. The descending kinetic efficiencies (β) of individual reactive species were defined as:

$$\beta_{\cdot OH} = k_{\cdot OH}/k \approx (k - k_{TBA})/k$$

$$\beta_{SO_4^{\cdot -}} = k_{SO_4^{\cdot -}}/k \approx (k - k_{MeOH})/k - (k - k_{TBA})/k$$

$$\beta_{^1O_2} = k_{^1O_2}/k \approx (k - k_{FFA})/k$$

$$\beta_{\cdot O_2^-} = k_{\cdot O_2^-}/k \approx (k - k_{p-BQ})/k$$

where k is the apparent pseudo-first-order rate constant obtained without adding any scavenger, while k_{TBA}、k_{MeOH}、k_{FFA} and k_{p-BQ} are the apparent rate constants measured in the presence of TBA、MeOH、FFA and p-BQ, respectively.

Based on the descending kinetic efficiencies, the relative contributions (γ) of different reactive species were estimated using the following equations:

$$\gamma_{\cdot OH} = \beta_{\cdot OH}/(\beta_{\cdot OH} + \beta_{SO_4^{\cdot -}} + \beta_{\cdot O_2^-} + \beta_{^1O_2})$$

$$\gamma_{SO_4^{\cdot -}} = \beta_{SO_4^{\cdot -}}/(\beta_{\cdot OH} + \beta_{SO_4^{\cdot -}} + \beta_{\cdot O_2^-} + \beta_{^1O_2})$$

$$\gamma_{^1O_2} = \beta_{^1O_2}/(\beta_{\cdot OH} + \beta_{SO_4^{\cdot -}} + \beta_{\cdot O_2^-} + \beta_{^1O_2})$$

$$\gamma_{\cdot O_2^-} = \beta_{\cdot O_2^-}/(\beta_{\cdot OH} + \beta_{SO_4^{\cdot -}} + \beta_{\cdot O_2^-} + \beta_{^1O_2})$$

where γ represents the estimated relative contribution of each reactive species to SDZ degradation.

Text S7 EPR

A 30 μL aliquot of the reaction solution was mixed with 30 μL of 100 mM DMPO (prepared in ultrapure water) as a spin-trapping agent for hydroxyl and sulfate radicals. After thorough homogenization, an appropriate volume of the mixture was drawn into a capillary, which was then placed into a quartz tube and inserted into the EPR resonator cavity for signal acquisition. For singlet oxygen detection, 30 μL of the reaction sample was mixed with 50 μL of 100 mM TEMP, gently vortexed, and similarly loaded into a capillary. The capillary was then inserted into a quartz tube and placed in the EPR sample cavity for $^1O_2$ measurement. The measurement parameters were set as follows: a center field of 3500 G with a sweep width of 100 G, a microwave frequency of 9.82 GHz, and a microwave power of 6.325 mW. The modulation frequency and modulation amplitude were maintained at 100 kHz and 1.0 G, respectively. Each spectrum was recorded with a sweep time of 30.0 s.

Text S8 Boron leaching

After 60 min of reaction, an aliquot of the reaction mixture was transferred into a digestion vessel, acidified with concentrated HNO_3, and subjected to microwave-assisted digestion for 30 min. The digested solution was then filtered through a 0.45 μm aqueous-phase membrane and analysed for boron content using ICP-MS (Agilent 7700).

Figures

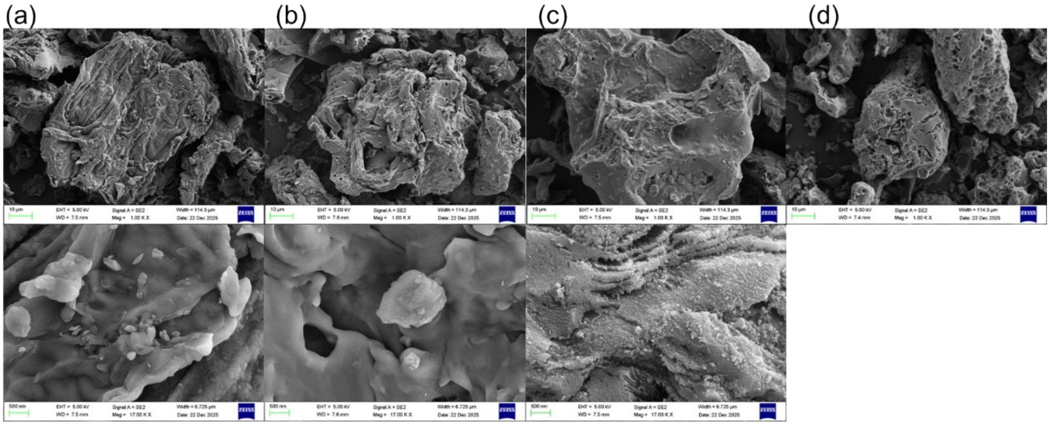


Fig. S1. SEM images of different biochar catalysts: (a) BC, (b) BBC, (c) SBC, (d)BS4C.

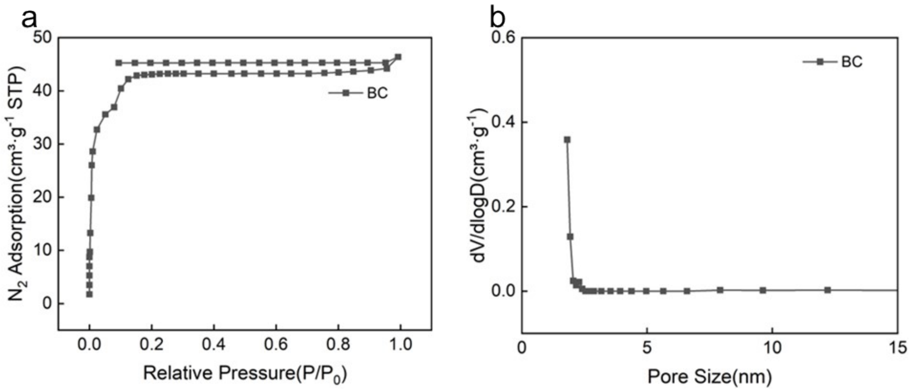


Fig.S2. (a)N_2 adsorption–desorption isotherms and (b) pore size distribution of BC

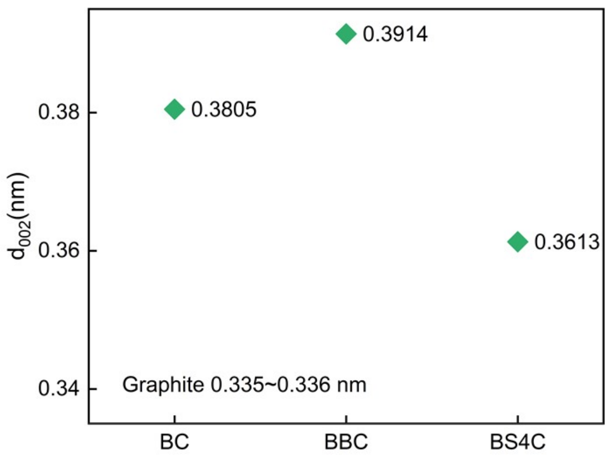


Fig. S3. The average interlayer spacing d_{002} of biochar samples

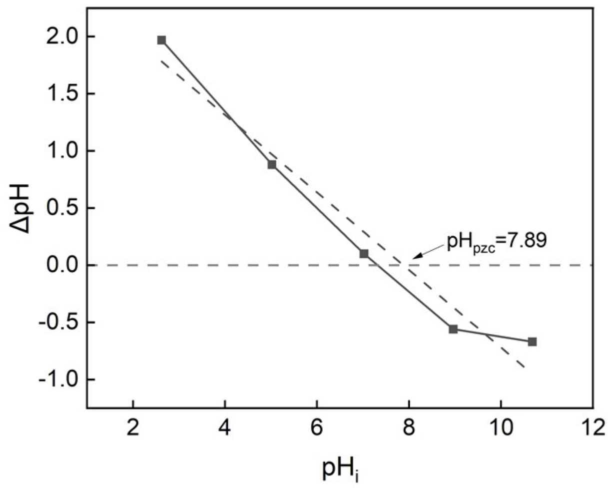
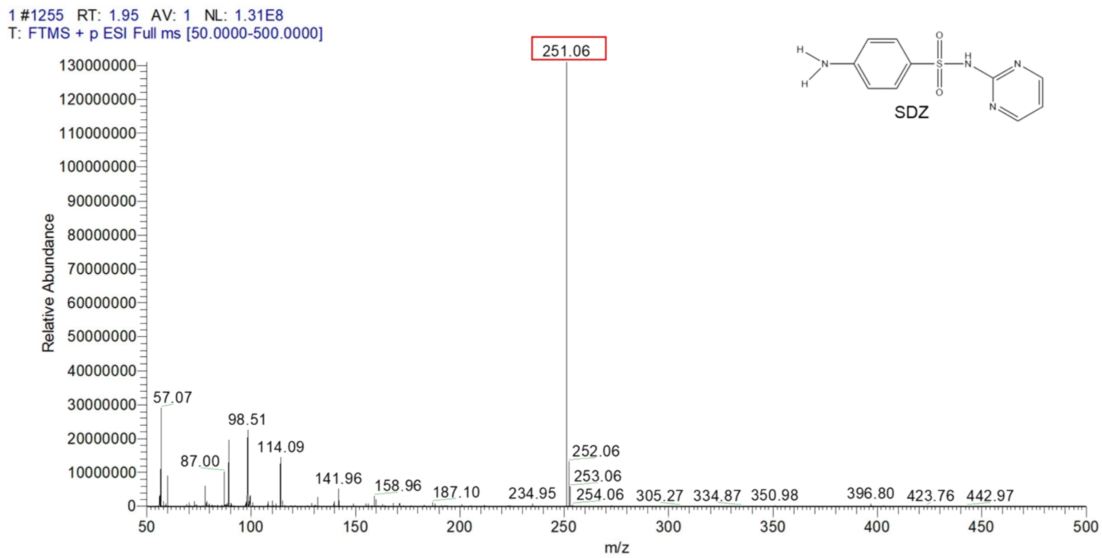
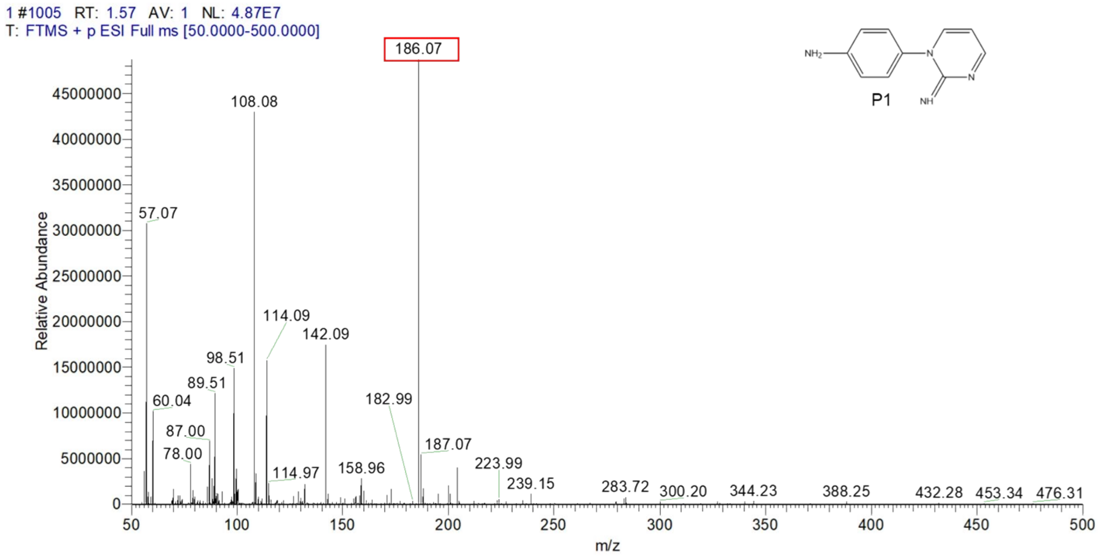
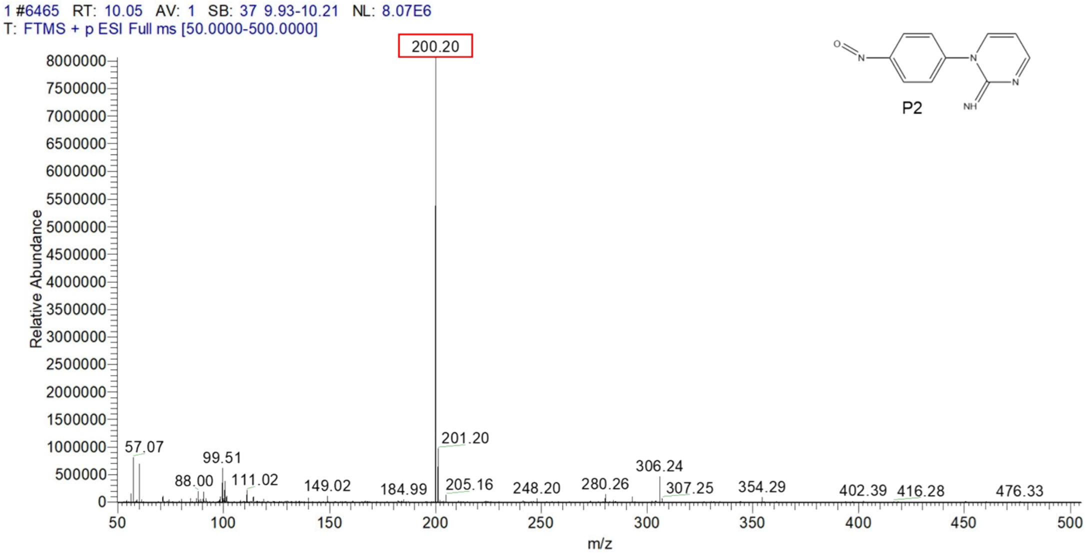


Fig. S4. pH$_{pzc}$ of BS4C.

Fig. S5. Mass spectrometer (MS) spectra of SDZ degradation intermediates in the BS4C/PDS system.



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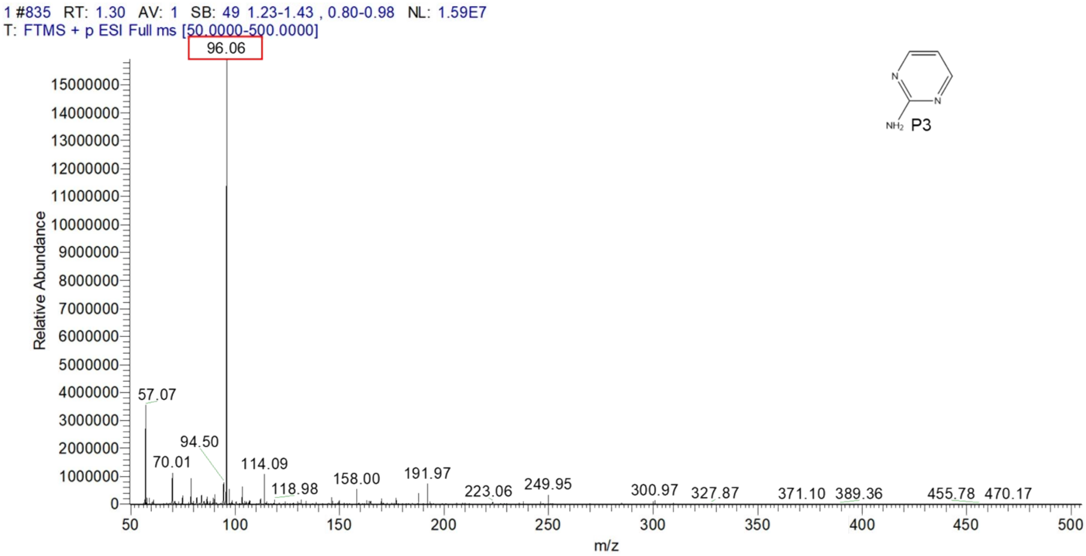
200.20
P2
Relative Abundance
m/z
57.07
88.00
99.51
111.02
149.02
184.99
201.20
205.16
248.20
280.26
306.24
307.25
354.29
402.39
416.28
476.33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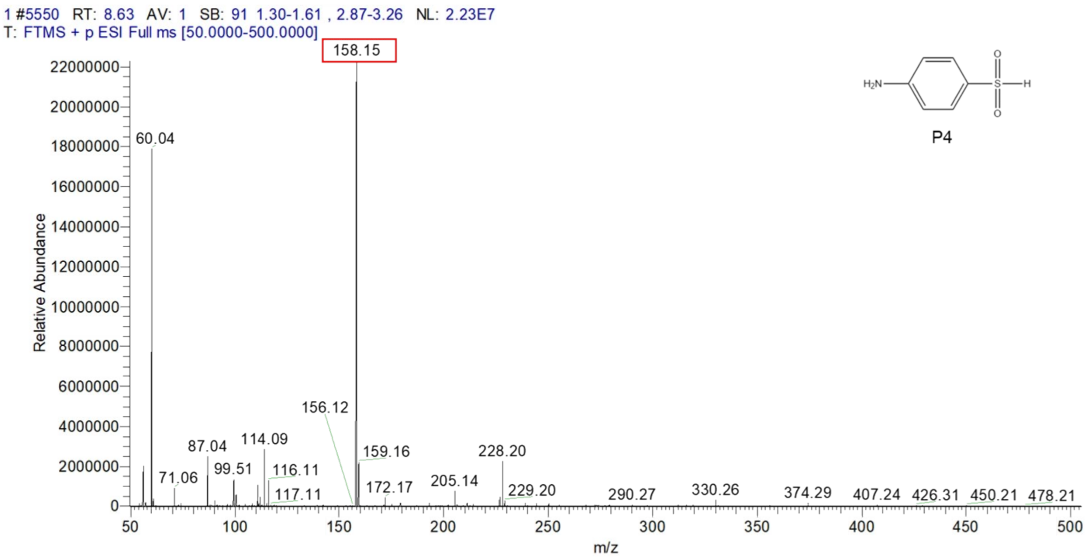
96.06
P3
Relative Abundance
m/z
57.07
70.01
94.50
114.09
118.98
158.00
191.97
223.06
249.95
300.97
327.87
371.10
389.36
455.78
470.17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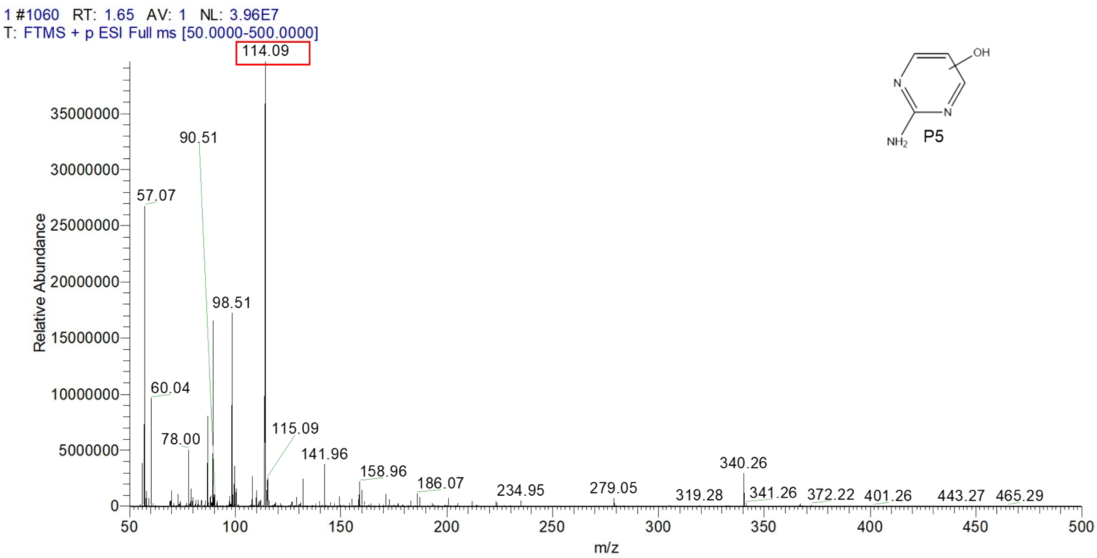
158.15
P4
Relative Abundance
m/z
60.04
71.06
87.04
99.51
114.09
116.11
117.11
156.12
159.16
172.17
205.14
228.20
229.20
290.27
330.26
374.29
407.24
426.31
450.21
478.21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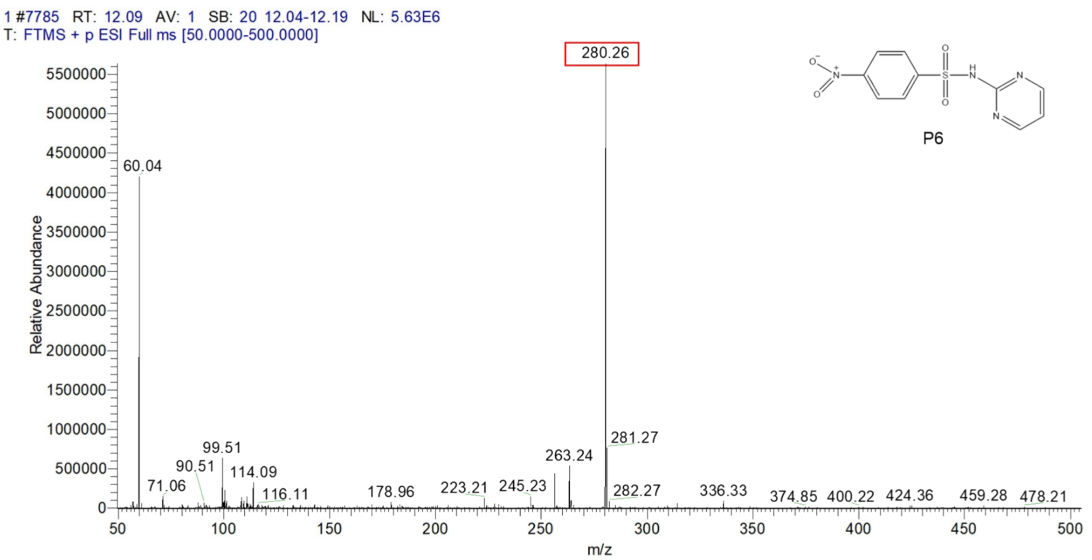
114.09
90.51
57.07
98.51
60.04
78.00
115.09
141.96
158.96
186.07
234.95
279.05
319.28
340.26
341.26
372.22
401.26
443.27
465.29
Relative Abundance
m/z
OH
N
N
NH2
P5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99.51
90.51
114.09
71.06
116.11
178.96
223.21
245.23
263.24
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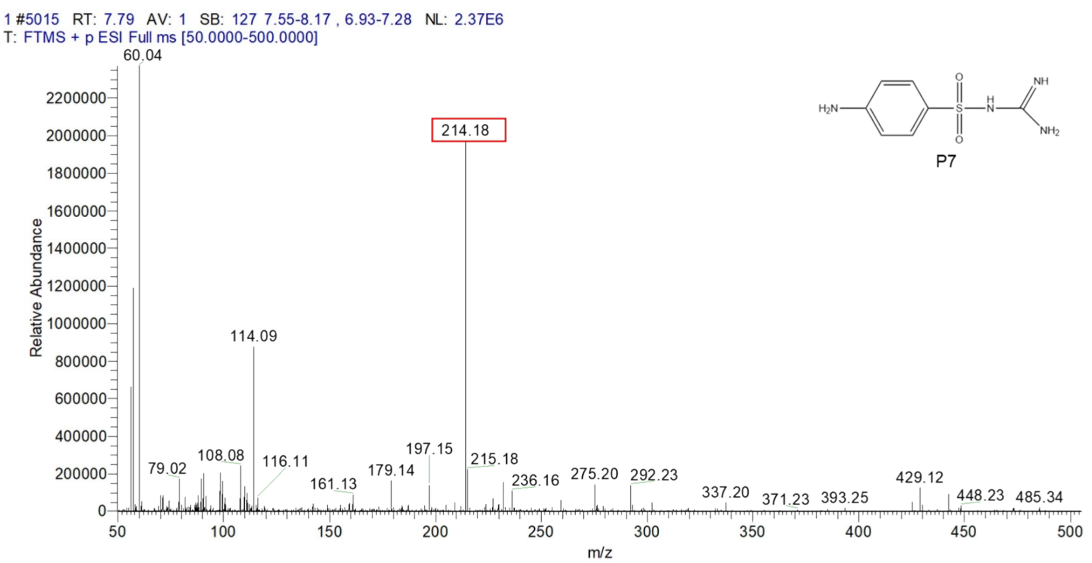
336.33
374.85
400.22
424.36
459.28
478.21
Relative Abundance
m/z
P6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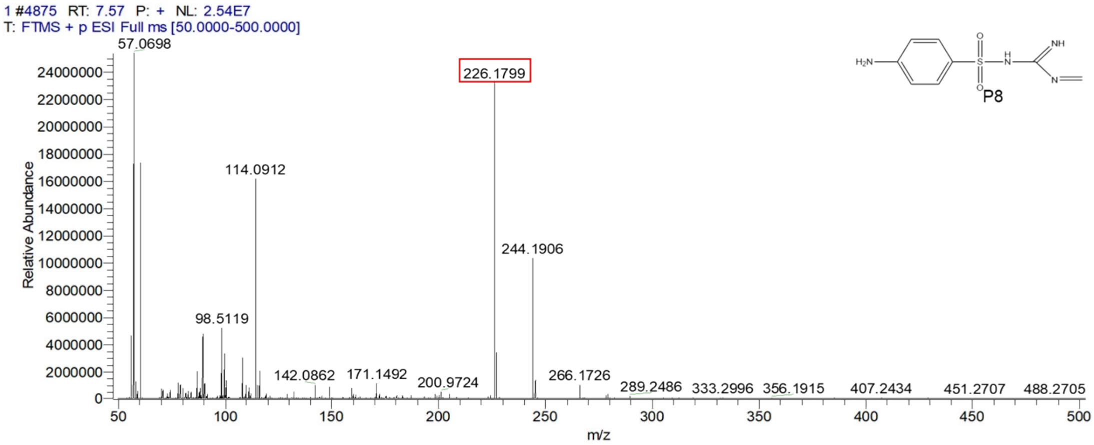
60.04
214.18
114.09
79.02
108.08
116.11
161.13
179.14
197.15
215.18
236.16
275.20
292.23
337.20
371.23
393.25
429.12
448.23
485.34
Relative Abundance
m/z
H2N
NH
NH2
P7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57.0698
226.1799
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142.0862
171.1492
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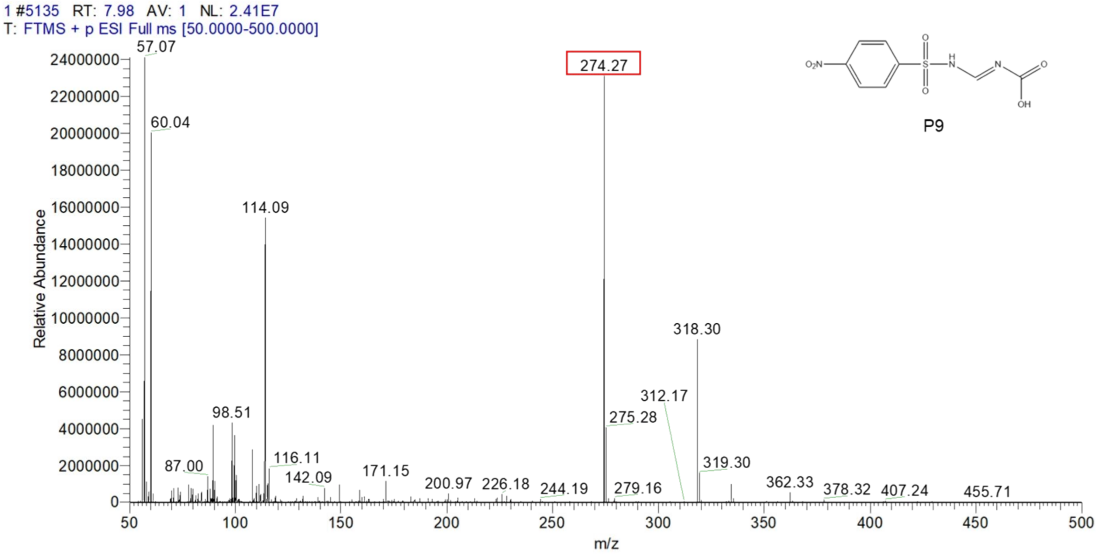
356.1915
407.2434
451.2707
488.2705
Relative Abundance
m/z
P8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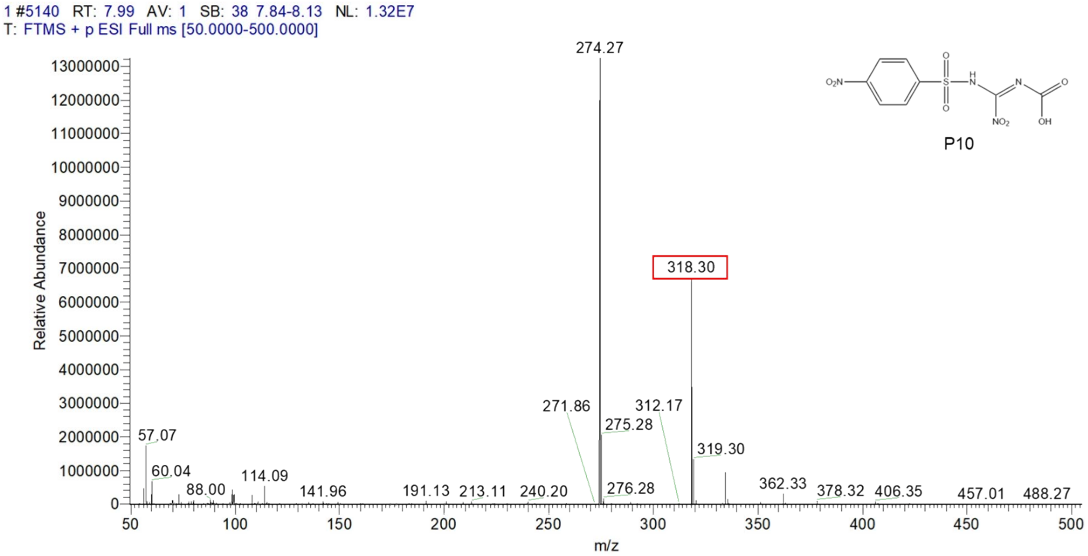
60.04
274.27
114.09
318.30
312.17
275.28
98.51
116.11
87.00
142.09
171.15
200.97
226.18
244.19
279.16
319.30
362.33
378.32
407.24
455.71
Relative Abundance
m/z
P9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271.86
312.17
275.28
319.30
57.07
60.04
88.00
114.09
141.96
191.13
213.11
240.20
276.28
362.33
378.32
406.35
457.01
488.27
Relative Abundance
m/z
P10

1 H. Zhao, L. Liu, B. Lu, M. Wu, H. Lu, J. Kang, J. Su, X. Jiang, Y. Wang, H. Miao, H. Zhu, Y. Dong and Y. Zhu, *Appl. Catal. B Environ. Energy*, 2025, **377**, 125498.