*Supplementary Materials*

# Visible-Light Activation of Persulfate or $H_2O_2$ by $Fe_2O_3/TiO_2$ Immobilized on Glass Support for Photocatalytic Removal of Amoxicillin: Mechanism, Transformation Products, and Toxicity Assessment

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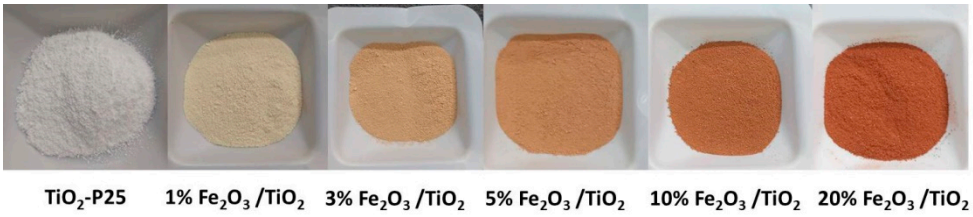



**Figure S1.** Photo images of $TiO_2$ (P25) and $TiO_2/Fe_2O_3$ nanocomposites

**Table S1.** FFD matrix for AMX removal rate constants ($k_{obs}$) by vis-(5% $Fe_2O_3/TiO_2$)/PS process after 150 min treatment

| Exp. # | Variables | | Experimental results | Response, *Y* |
|---|---|---|---|---|
| | $X_1$ | $X_2$ | | |
| | coded | coded | $k_{obs}$(AMX), × $10^{-7}$ M $min^{-1}$ | |
| 1 | -1 | -1 | 1.29 | 1.31 |
| 2 | 0 | -1 | 1.27 | 1.23 |
| 3 | 1 | -1 | 0.65 | 0.66 |
| 4 | -1 | 0 | 1.48 | 1.46 |
| 5 | 0 | 0 | 1.40 | 1.41 |
| 6 | 1 | 0 | 0.87 | 0.87 |
| 7 | -1 | 1 | 1.35 | 1.34 |
| 8 | 0 | 1 | 1.30 | 1.32 |
| 9 | 1 | 1 | 0.82 | 0.81 |

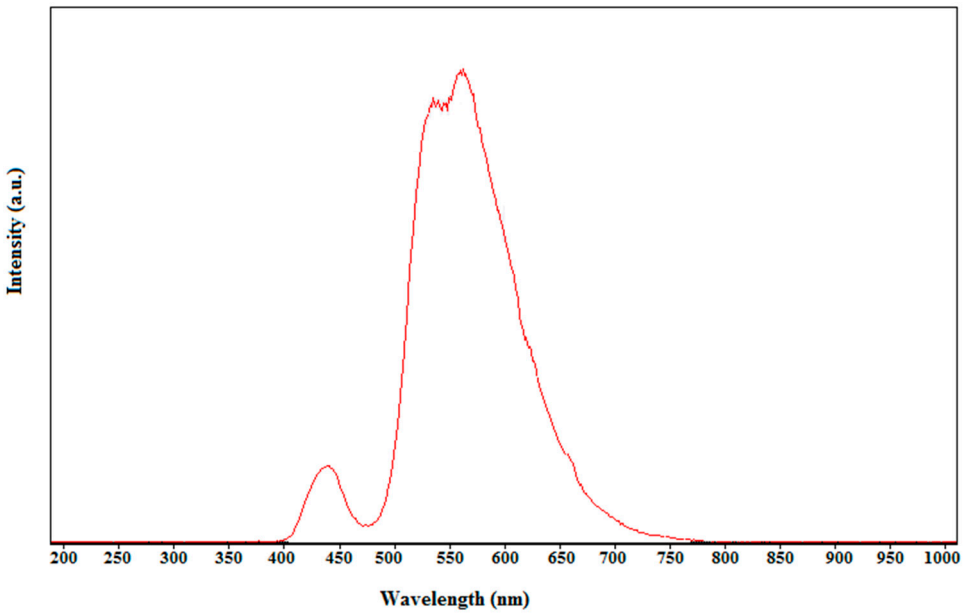
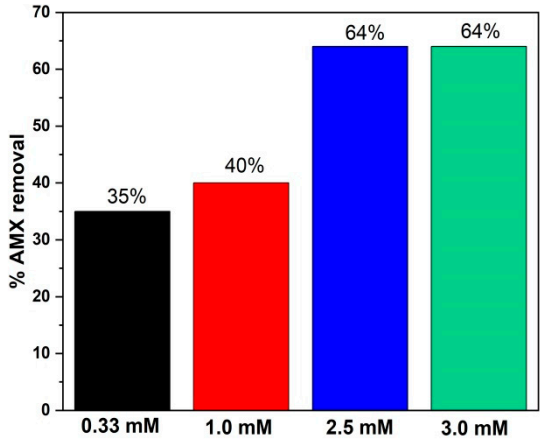



**Figure S2.** Full Spectrum Coverage of LED used in PEC tests




**(a)** **(b)**

**Figure S3.** Photocatalytic removal of AMX using prepared 5%$Fe_2O_3$/$TiO_2$ under visible light irradiation with different PS concentration; (a) removal profile and (b) % removal per different PS concentration(*Conditions:* [catalyst dosage]= 0.5 g/L ; [AMX]= 0.05 mM ; initial pH = natural pH (5.5))

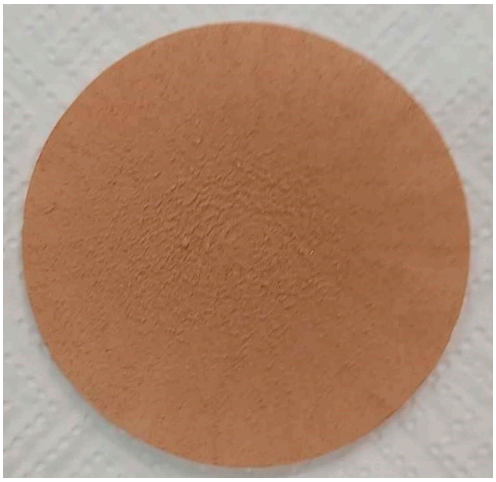


**Figure S4.** Photo image of immobilized 5% $Fe_2O_3$/$TiO_2$ nanocomposite onto glass support

**Table S2.** Analysis of variance (ANOVA) of RSM model predicting AMX removal rate constants ($k_{obs}$) by vis-(5% $Fe_2O_3/TiO_2$)/PS process after 150 min treatment

| Factor (coded) | Statistical analysis | | | | |
|---|---|---|---|---|---|
| | SS | df | MSS | *F* | *p* |
| Model | 0.7014 | 5 | 0.1403 | 136.37 | 0.0010* |
| $X_1$ | 0.5281 | 1 | 0.5281 | 513.33 | 0.0002* |
| $X_1^2$ | 0.1217 | 1 | 0.1217 | 118.29 | 0.0017* |
| $X_2$ | 0.0113 | 1 | 0.0113 | 10.95 | 0.0454* |
| $X_2^2$ | 0.0374 | 1 | 0.0374 | 36.31 | 0.0092* |
| $X_1 \times X_2$ | 0.0030 | 1 | 0.0030 | 2.94 | 0.1849 |
| Residual | 0.0031 | 3 | 0.0010 | | |
| Total | 0.7045 | 8 | | | |

*$p$<0.05 means that model or model term is significant

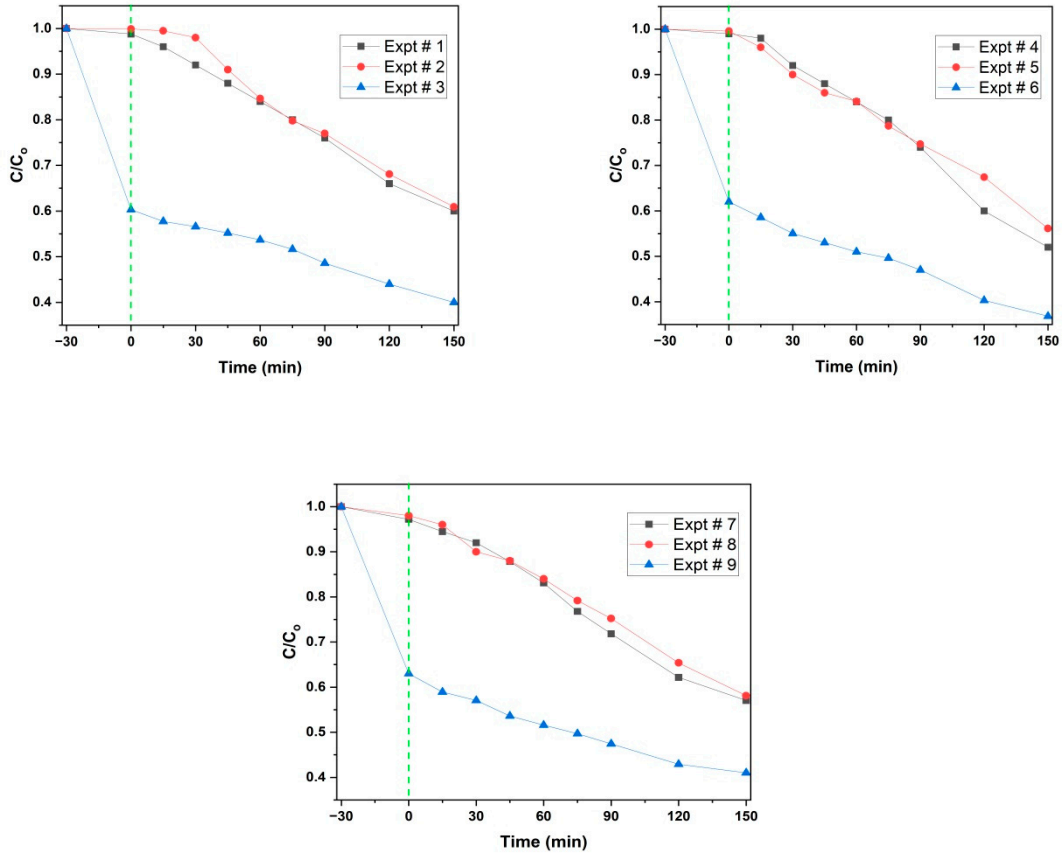
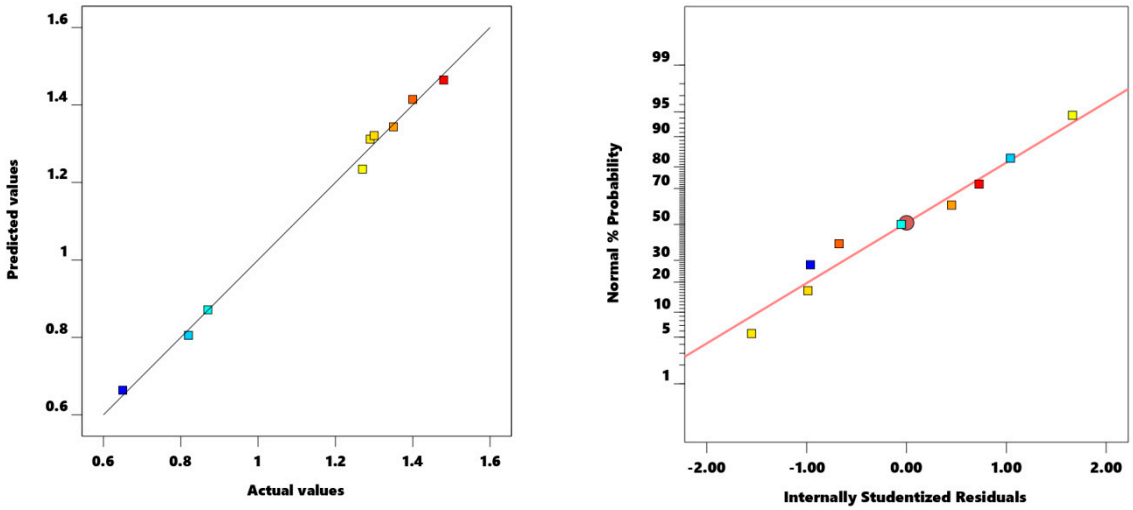


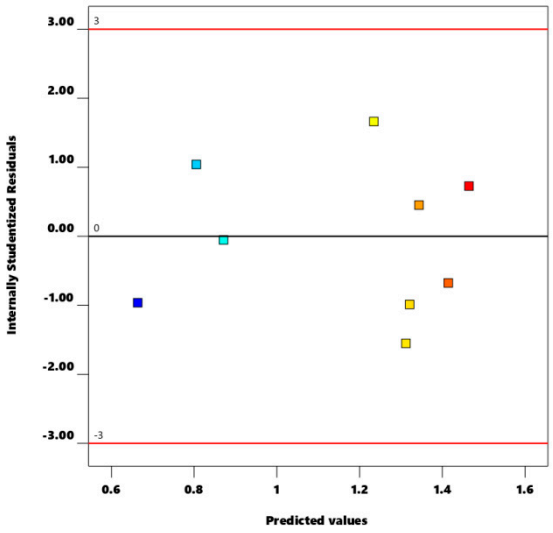

**Figure S5.** AMX photocatalytic treatment by vis-(5% $Fe_2O_3/TiO_2$)/PS. Experimental conditions set by FFD (Table S1, Supplementary material)




(**a**)



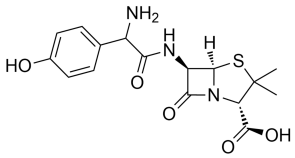
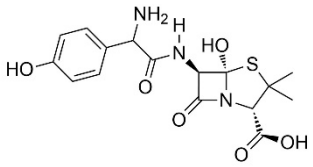

(**b**)

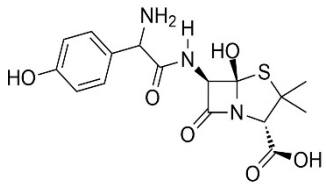
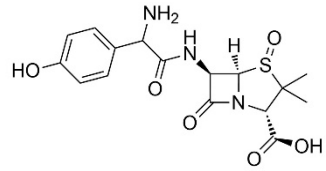
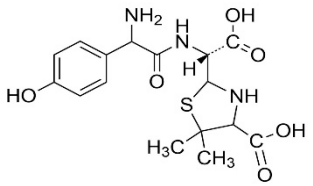
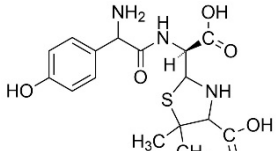


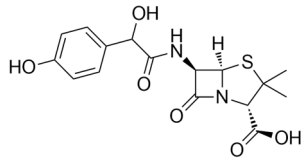
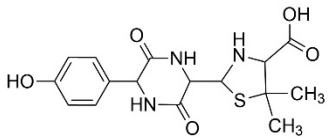

(**c**)

**Figure S6.** Residual diagnostics of RSM model predicting AMX removal rate constants ($k_{obs}$) by vis-(5% $Fe_2O_3/TiO_2$)/PS process after 150 min treatment: (A) observed *vs.* predicted plot, (B) normal probability plot, and (C) internally studentized residuals *vs.* predicted values plot

**Table S3.** Accurate mass measurements found by LC-MS-Orbitrap of protonated AMX conversion products and their corresponding fragment ions

| $R_t$ (min) | Compound | Chemical Formula | m/z (Experimental) | RDBE | Annotated Δmass (ppm) | FISh Coverage | Suggested chemical structure | Photocatalysis | Photocatalysis + $H_2O_2$ | Photocatalysis + Persulfate | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.180 | **AMX** | $C_{16}H_{20}N_3O_5S$ [M+H]$^+$ | 366.11102 | 8.5 | | | | | | | [1,2] |
| | | $C_{16}H_{17}N_2O_5S$ [M+H–($NH_3$)]$^+$ | 349.08459 | 9.5 | | | | | | | |
| | | $C_{15}H_{17}N_2O_4S$ | 321.09079 | 8.5 | -1.68 | 64.71 |  | ---- | ---- | ---- | |
| | | $C_{11}H_8NO_3S$ | 234.02155 | 8.5 | | | | | | | |
| | | $C_{10}H_{10}NO_2S$ | 208.04260 | 6.5 | | | | | | | |
| | | $C_6H_{10}NO_2S$ | 160.04242 | 2.5 | | | | | | | |
| | | $C_4H_4NOS$ | 114.00060 | 3.5 | | | | | | | |
| 0.397 | **TP 382** | $C_{16}H_{20}N_3O_6S$ [M+H]$^+$ | 382.10617 | 8.5 | - | | | | | | |
| | **(E1)** | $C_{16}H_{17}N_2O_6S$ [M+H–($NH_3$)]$^+$ | 365.07965 | 9.5 | | | | | | | Proposed |
| | | $C_{10}H_9N_2O_2$ | 189.06583 | 7.5 | | | | *X* | ✓ | ✓ | Structure |
| | | $C_9H_8NO_2$ | 162.05482 | 6.5 | -1.48 | 43.75 |  | | | | |
| | | $C_5H_{10}NO_2S$ | 148.04237 | 1.5 | | | | | | | |
| | | $C_5H_7O_2S$ | 131.01610 | 2.5 | | | | | | | |
| | | $C_5H_5OS$ | 113.00550 | 3.5 | | | | | | | |
| | | $C_7H_7O$ | 107.04916 | 4.5 | | | | | | | |
| 0.532 | **TP 382** | $C_{16}H_{20}N_3O_6S$ [M+H]$^+$ | 382.10614 | 8.5 | - | | | | | | Proposed |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **(E2)** | $C_{16}H_{17}N_2O_6S$ [M+H–$(NH_3)$]$^+$ | 365.07974 | 9.5 | -1.46 | 56.67 |  | X | ✓ | ✓ | Structure |
| | | $C_{10}H_9N_2O_2$ | 189.06616 | 7.5 | | | | | | | |
| | | $C_9H_8NO_2$ | 162.05492 | 6.5 | | | | | | | |
| | | $C_5H_{10}NO_2S$ | 148.04259 | 1.5 | | | | | | | |
| | | $C_5H_7O_2S$ | 131.01564 | 2.5 | | | | | | | |
| | | $C_5H_5OS$ | 113.00517 | 3.5 | | | | | | | |
| | | $C_7H_7O$ | 107.04927 | 4.5 | | | | | | | |
| 0.929 | **TP 382** | $C_{16}H_{20}N_3O_6S$ [M+H]$^+$ | 382.10602 | 8.5 | | | | | | | [3][4,5] |
| | **(S-O)** | $C_{16}H_{17}N_2O_6S$ [M+H–$(NH_3)$]$^+$ | 365.07938 | 9.5 | | | | | | | |
| | | $C_{15}H_{17}N_2O_5$ | 337.08368 | 8.5 | -1.44 | 100.00 |  | X | ✓ | ✓ | |
| | | $C_9H_9N_2O$ | 161.07129 | 6.5 | | | | | | | |
| 1.106 | **TP384 (H1)** | $C_{16}H_{22}N_3O_6S$ [M+H]$^+$ | 384.12177 | 7.5 | -1.71 | 72.73 | | | | | [2] |
| | | $C_{16}H_{19}N_2O_6S$ [M+H–$(NH_3)$]$^+$ | 367.09509 | 8.5 | | |  | ✓ | ✓ | ✓ | |
| | | $C_{15}H_{19}N_2O_4S$ | 323.10626 | 7.5 | | | | | | | |
| | | $C_7H_{13}N_2O_4S$ | 189.06905 | 2.5 | | | | | | | |
| | | $C_6H_{10}NO_2S$ | 160.04237 | 2.5 | | | | | | | |
| 1.146 | **TP384 (H2)** | $C_{16}H_{22}N_3O_6S$ [M+H]$^+$ | 384.12170 | 7.5 | -1.90 | 80.00 |  | | | | [2] |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $C_{16}H_{19}N_2O_6S$ [M+H–($NH_3$)]$^+$ | 367.09537 | 8.5 | | | | | | | |
| | | $C_{15}H_{19}N_2O_4S$ | 323.10568 | 7.5 | | | | | ✓ | ✓ | ✓ |
| | | $C_7H_{13}N_2O_4S$ | 189.06898 | 2.5 | | | | | | | |
| | | $C_6H_{10}NO_2S$ | 160.04245 | 2.5 | | | | | | | |
| 1.200 | **TP367** | $C_{16}H_{19}N_2O_6S$ [M+H]$^+$ | 367.11459 | 7.5 | -1.70 | 66.67 | | | | | |
| | | $C_{16}H_{17}N_2O_5S$ [M+H–($H_2O$)]$^+$ | 349.08456 | 8.5 | | |  | | | | Proposed |
| | | $C_{11}H_8NO_3S$ | 234.02122 | 8.5 | | | | | ✓ | ✓ | *X* Structure |
| | | $C_6H_{10}NO_2S$ | 160.04240 | 2.5 | | | | | | | |
| | | $C_4H_4NOS$ | 114.00066 | 3.5 | | | | | | | |
| 1.669 | **TP366** | $C_{16}H_{20}N_3O_5S$ [M+H]$^+$ | 366.11102 | 8.5 | -1.83 | 66.67 |  | | | | [2] |
| | | $C_{10}H_{11}N_2O_3$ | 207.07625 | 6.5 | | | | | | | |
| | | $C_6H_{10}NO_2S$ | 160.04257 | 2.5 | | | | | ✓ | ✓ | ✓ |
| | | $C_5H_8NS$ | 114.03694 | 2.5 | | | | | | | |

References

[1] J.B. Arsand, R.B. Hoff, L. Jank, L.N. Meirelles, M. Silvia Díaz-Cruz, T.M. Pizzolato, D. Barceló, Transformation products of amoxicillin and ampicillin after photolysis in aqueous matrices: Identification and kinetics, Sci. Total Environ. 642 (2018) 954–967. https://doi.org/10.1016/j.scitotenv.2018.06.122.

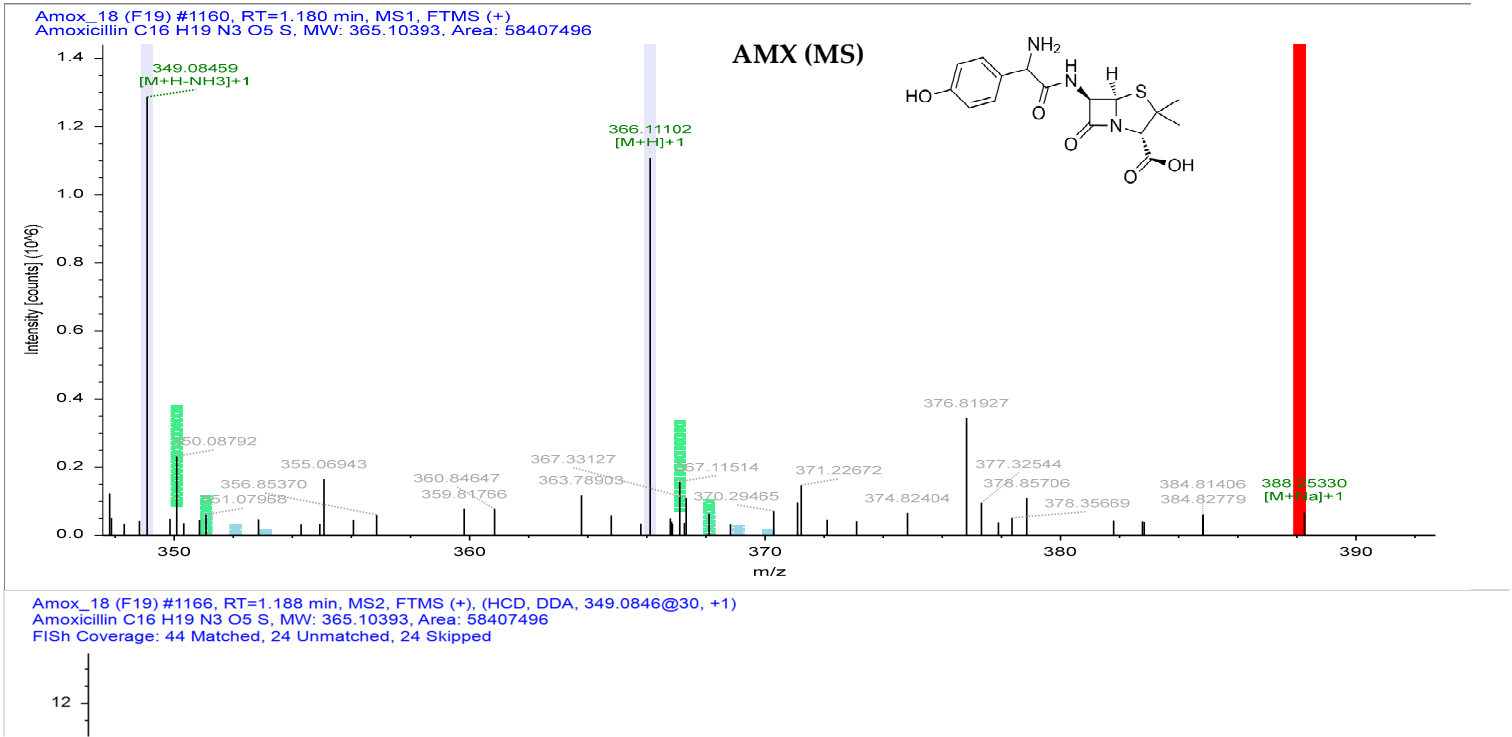
[2] A.G. Trovó, R.F. Pupo Nogueira, A. Agüera, A.R. Fernandez-Alba, S. Malato, Degradation of the antibiotic amoxicillin by photo-Fenton process - Chemical and

toxicological assessment, Water Res. 45 (2011) 1394–1402. https://doi.org/10.1016/j.watres.2010.10.029.

[3] Y. Zhang, Y. Xiao, Y. Zhong, T.T. Lim, Comparison of amoxicillin photodegradation in the UV/H2O2 and UV/persulfate systems: Reaction kinetics, degradation pathways, and antibacterial activity, Chem. Eng. J. 372 (2019) 420–428. https://doi.org/10.1016/j.cej.2019.04.160.

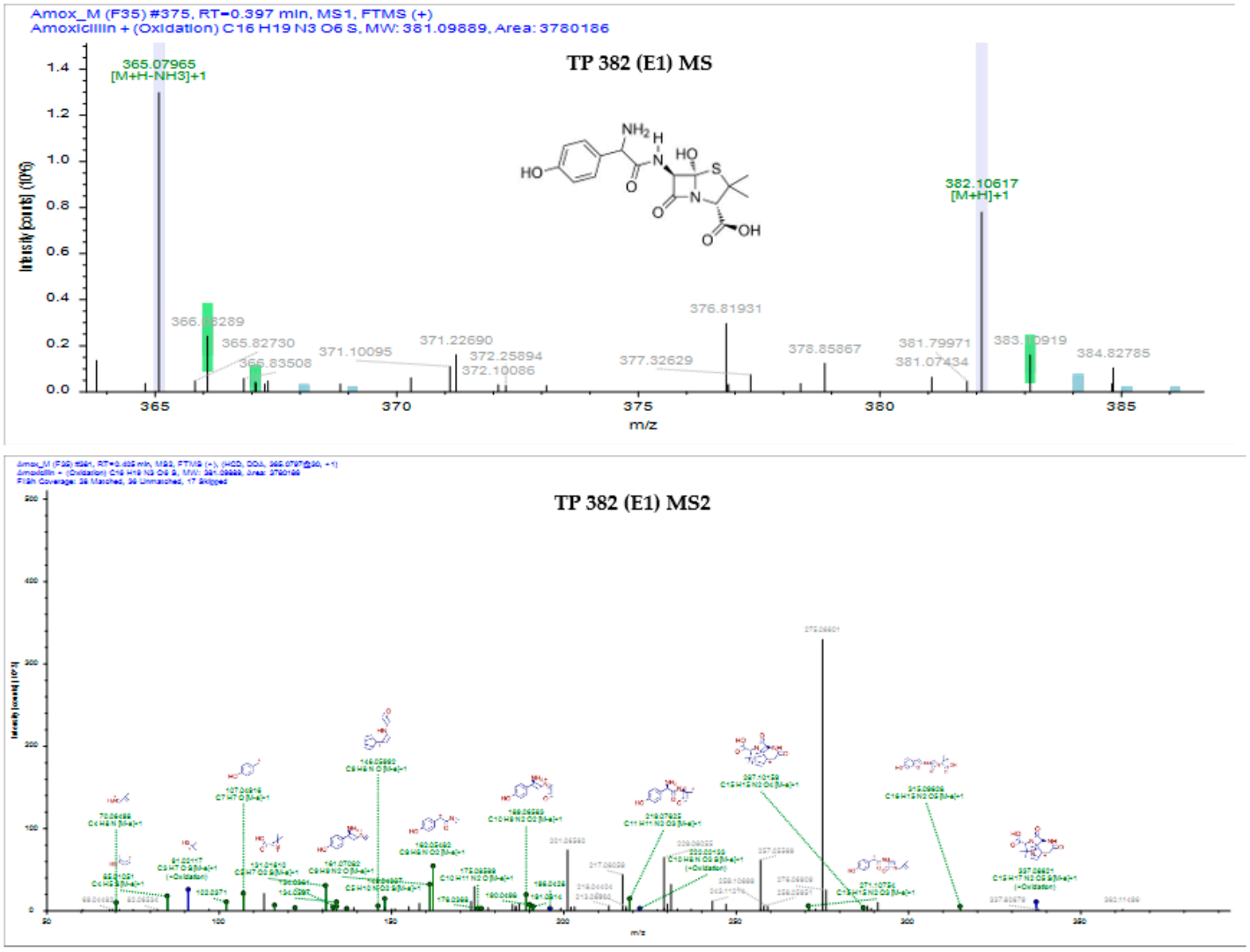
[4] I. Gozlan, A. Rotstein, D. Avisar, Investigation of an amoxicillin oxidative degradation product formed under controlled environmental conditions, Environ. Chem. 7 (2010) 435–442. https://doi.org/10.1071/EN10037.

[5] I. Gozlan, A. Rotstein, D. Avisar, Amoxicillin-degradation products formed under controlled environmental conditions: Identification and determination in the aquatic environment, Chemosphere. 91 (2013) 985–992. https://doi.org/10.1016/j.chemosphere.2013.01.095.

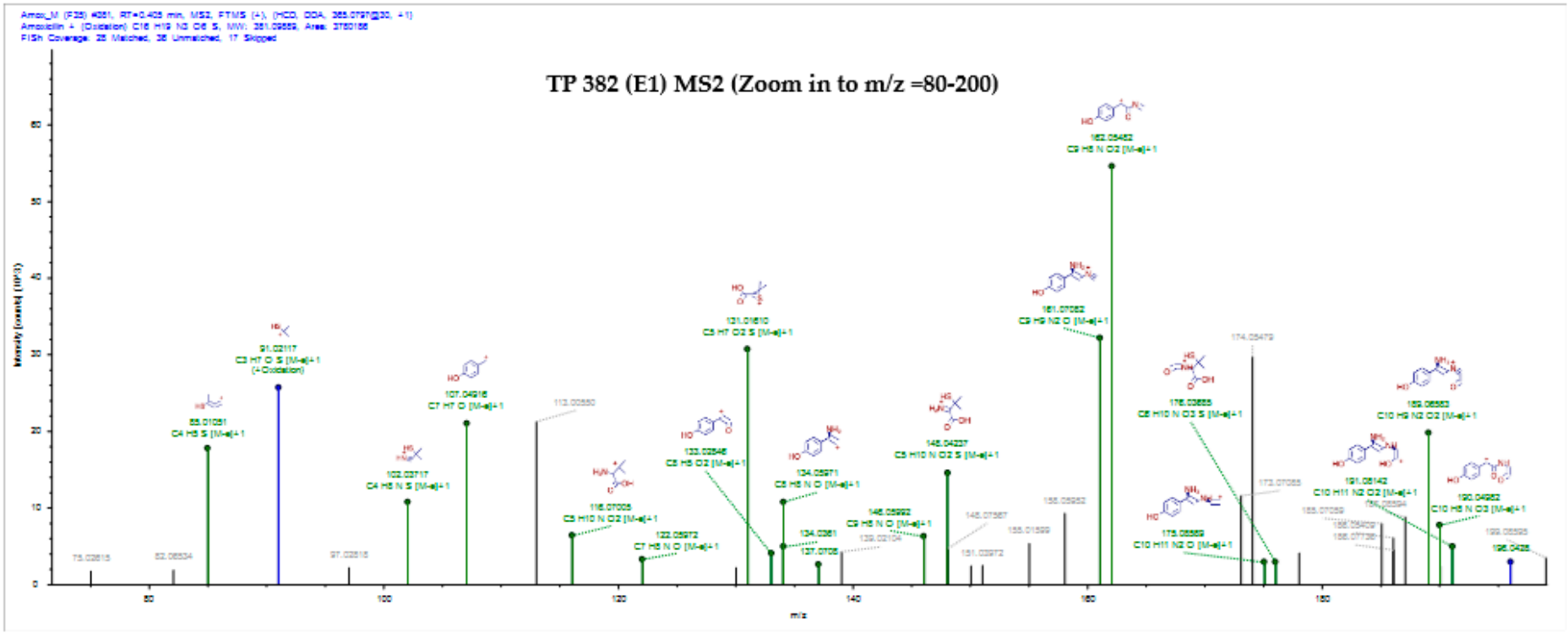


**AMX (MS 2)**

**Figure S7.** MS and MS spectra of AMX


Amox_M (F35) #375, RT=0.397 min, MS1, FTMS (+)
Amoxicillin + (Oxidation) C16 H19 N3 O6 S, MW: 381.09889, Area: 3780186
TP 382 (E1) MS
365.07965
[M+H-NH3]+1
382.10617
[M+H]+1
Intensity [counts] (10^6)
m/z
TP 382 (E1) MS2

(**a**)




(**b**)

**Figure S8. (a)**MS and MS spectra of TP 382 (E1); (b) MS2 spectrum (magnified) of TP 382 (E1)

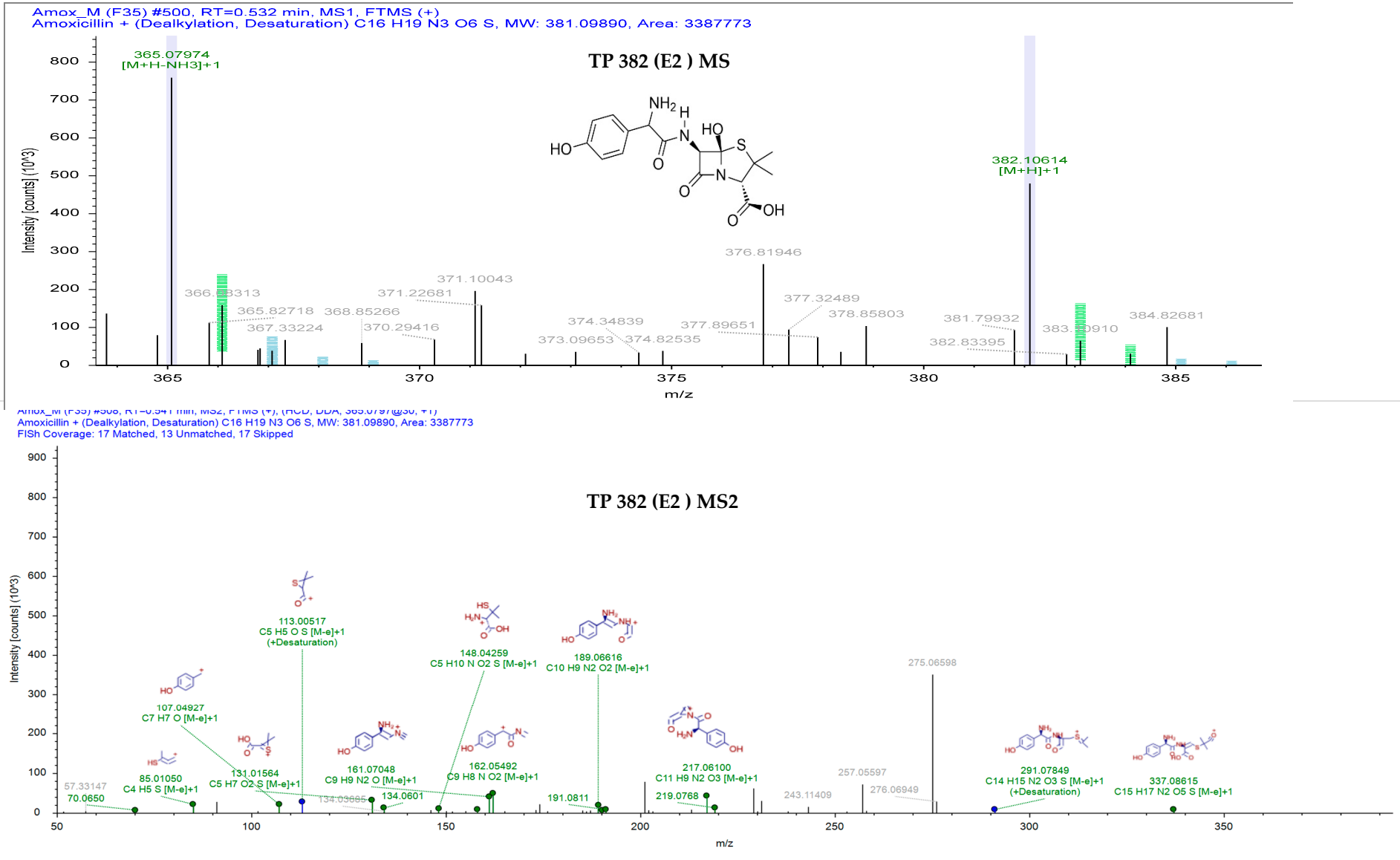
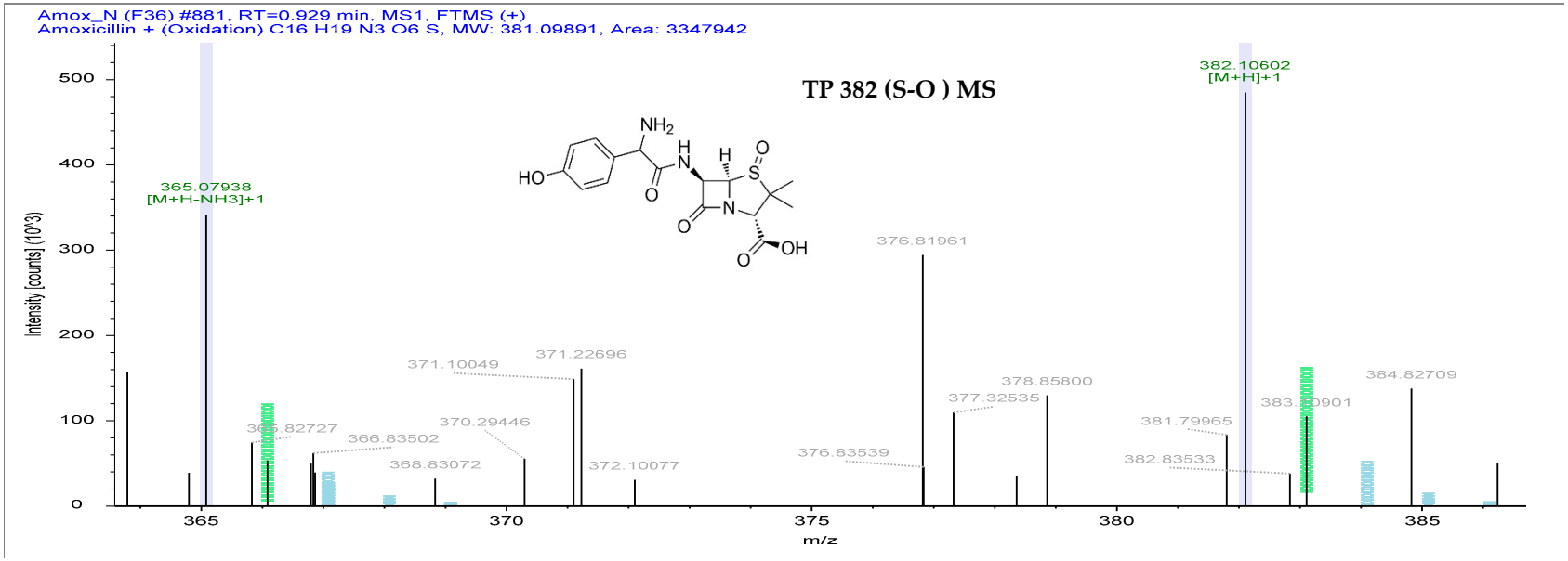



**Figure S9.** MS and MS2 spectra of TP 382 (E2)



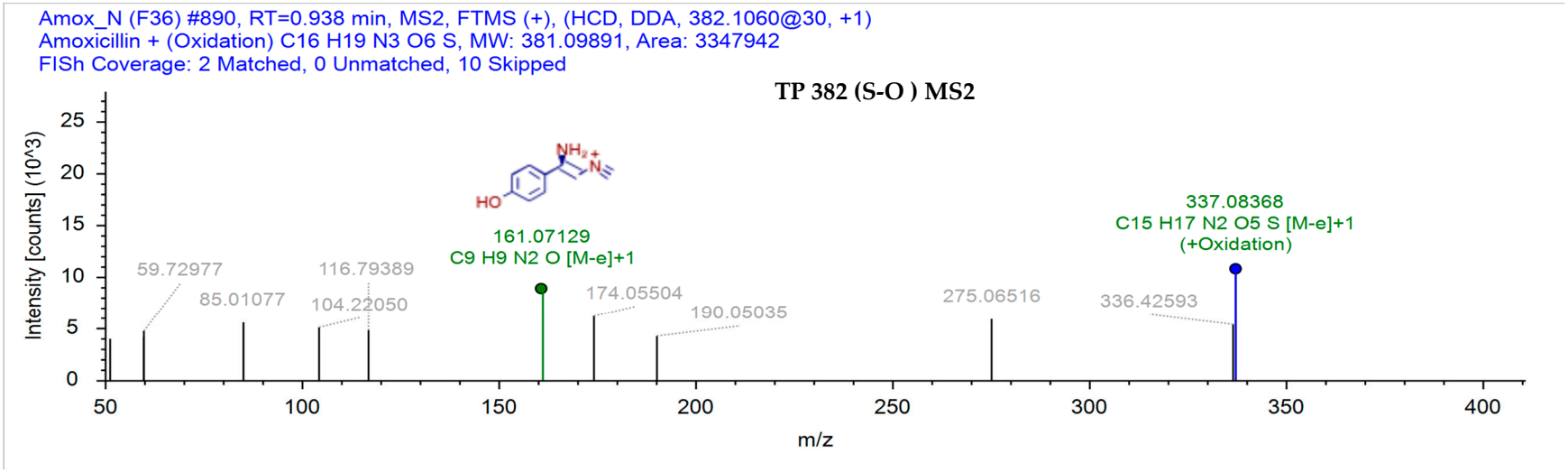




**Figure S10.** MS and MS2 spectra of TP 382 (S-O)

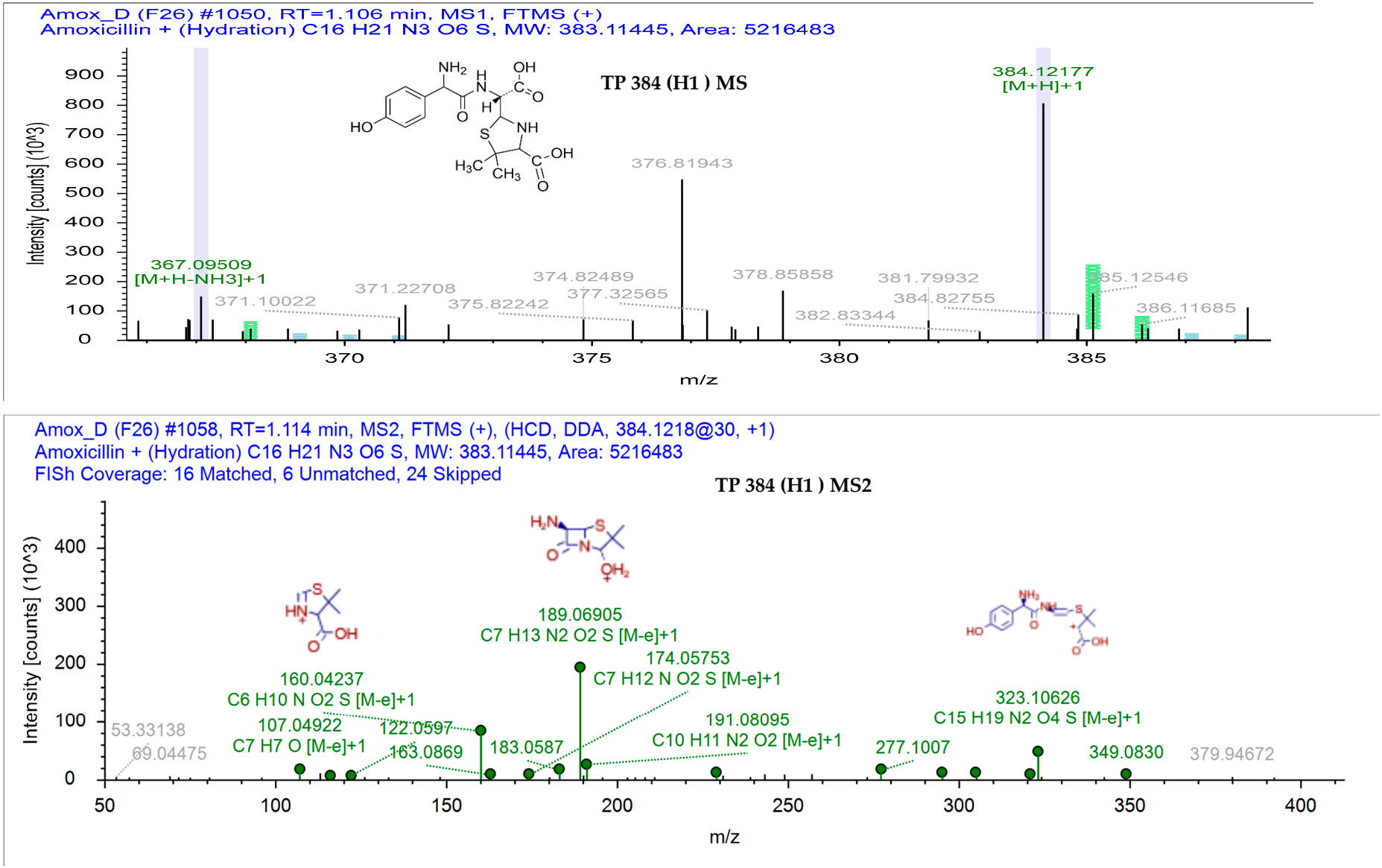
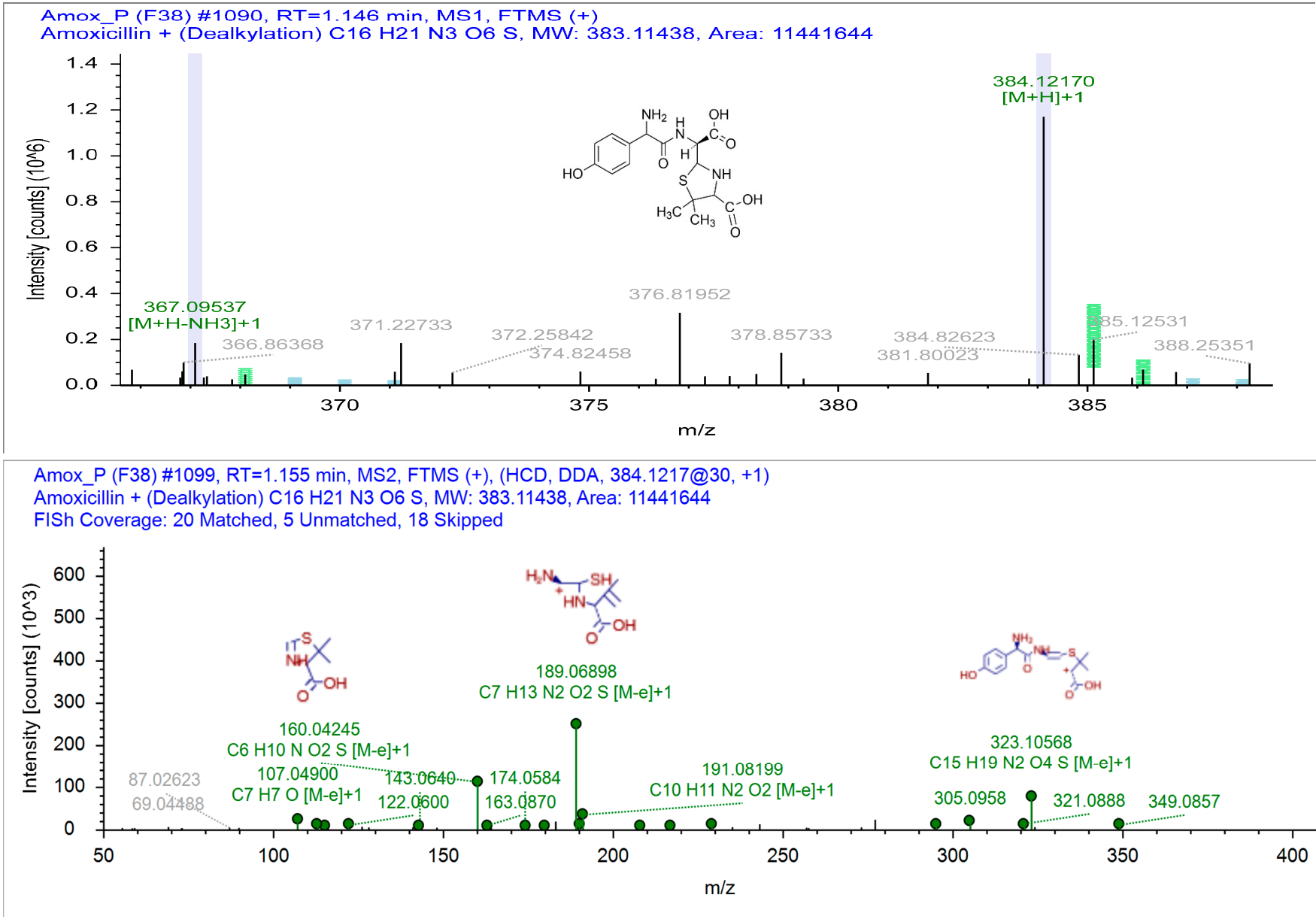



**Figure S11.** MS and MS2 spectra of TP 384 (H1)


Amox_P (F38) #1090, RT=1.146 min, MS1, FTMS (+)
Amoxicillin + (Dealkylation) C16 H21 N3 O6 S, MW: 383.11438, Area: 11441644
Intensity [counts] (10^6)
m/z
384.12170
[M+H]+1
367.09537
[M+H-NH3]+1
366.86368
371.22733
372.25842
374.82458
376.81952
378.85733
381.80023
384.82623
385.12531
388.25351
Amox_P (F38) #1099, RT=1.155 min, MS2, FTMS (+), (HCD, DDA, 384.1217@30, +1)
Amoxicillin + (Dealkylation) C16 H21 N3 O6 S, MW: 383.11438, Area: 11441644
FISh Coverage: 20 Matched, 5 Unmatched, 18 Skipped
Intensity [counts] (10^3)
m/z
189.06898
C7 H13 N2 O2 S [M-e]+1
160.04245
C6 H10 N O2 S [M-e]+1
107.04900
C7 H7 O [M-e]+1
87.02623
69.04488
143.0640
122.0600
174.0584
163.0870
191.08199
C10 H11 N2 O2 S [M-e]+1
323.10568
C15 H19 N2 O4 S [M-e]+1
305.0958
321.0888
349.0857