Supporting information

for

Orange peel biochar/clay/titania composites: low cost, high performance, and easy-to-reuse photocatalysts for the degradation of tetracycline in water

Morenike O. Adesina,[1,2,3,4] Moses O. Alfred,[2,3] Harald Seitz,[5] Katlen Brennenstuhl,[1] Harshadrai M. Rawel,[6] Pablo Wessig,[1] Jiyong Kim,[7] Armin Wedel,[7] Wouter Koopman,[8] Christina Günter,[9] Emmanuel I. Unuabonah,[2,3] and Andreas Taubert[1,*]

[1] Institute of Chemistry, University of Potsdam, D-14476 Potsdam, Germany.

[2] African Centre of Excellence for Water and Environment Research (ACEWATER), Redeemer's University, PMB 230, Ede, Osun State, Nigeria.

[3] Department of Chemical Sciences, Redeemer's University, PMB 230, Ede, Osun State, Nigeria.

[4] Lead City University, Ibadan, Oyo State, Nigeria.

[5] Fraunhofer Institute for Cell Therapy and Immunology, Branch Bioanalytics and Bioprocesses (IZI-BB), 14476 Potsdam, Germany.

[6] Institute of Nutritional Science, University of Potsdam, D-14558 Nuthetal Potsdam, Germany.

[7] Functional Materials and Devices, Fraunhofer Institute for Applied Polymer Research, Potsdam 14476 Potsdam, Germany

[8] Institute of Physics and Astronomy, University of Potsdam, D-14476 Potsdam, Germany

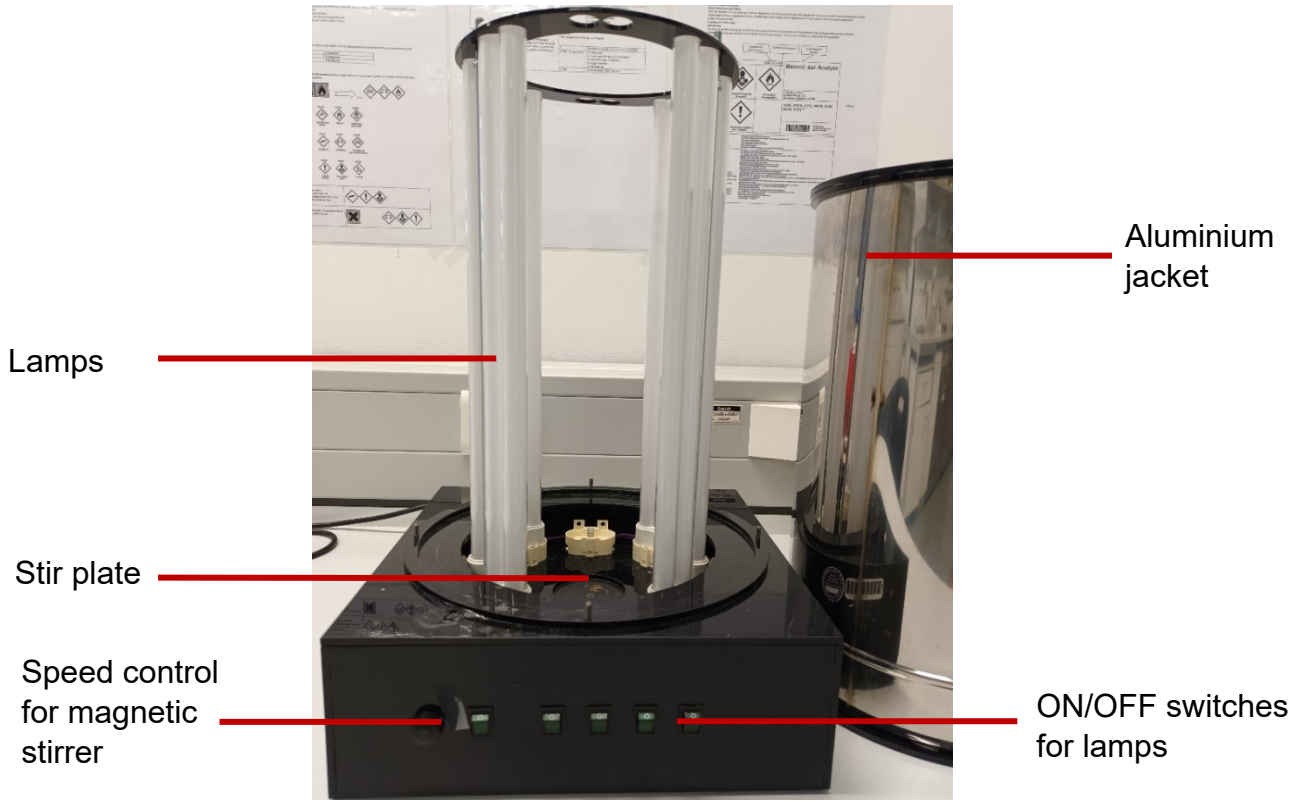
[9] Institute of Geosciences, University of Potsdam, D-14476 Potsdam, Germany.

* Corresponding author: ataubert@uni-potsdam.de

Material and Reagents.

Titanium tetra isopropoxide (98%), tetracycline (98%, Sigma-Aldrich), and ethanol (99.8%, Carl Roth) were used as received. Raw kaolin clay was obtained from Redemption City, Mowe (6°48′0″N, 3°26′0″E.), Ogun State, Nigeria. Orange peel (OP) was sourced from the local REWE supermarket in Potsdam-Golm, Germany. NaCl, Na_2SO_4 (Merck), $NaHCO_3$ (Fisher), NaOH (Merck), Isopropanol (VWR), benzoquinone (Sigma-Aldrich), sodium oxalate (Sigma-Aldrich).

Photoreactor setup



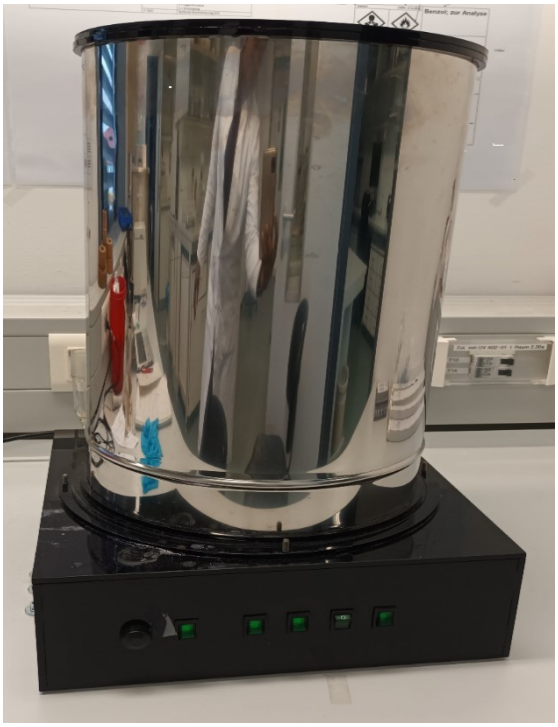


Figure S1. Homebuilt photoreactor: top image open and bottom image with the reflective jacket mounted.

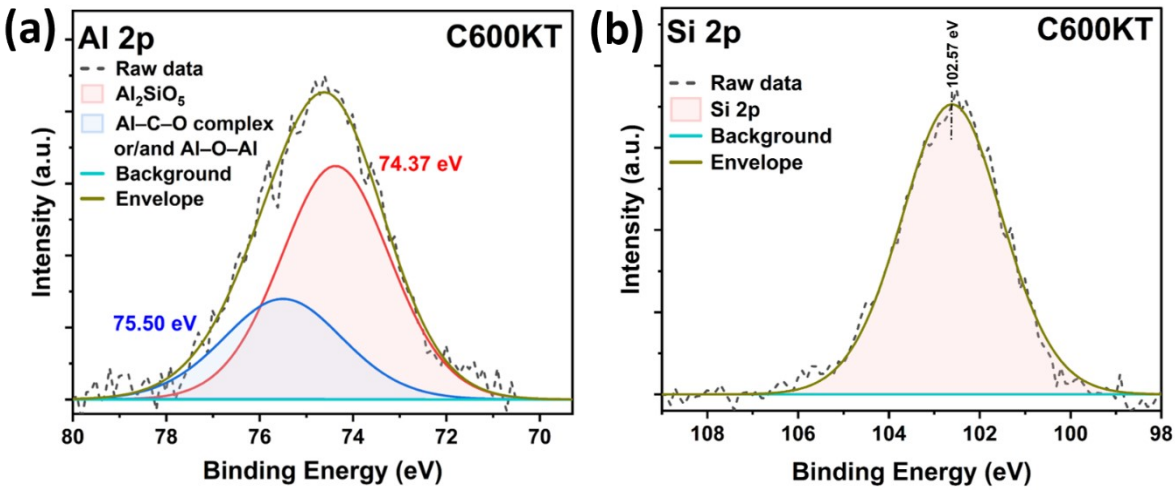


Figure S2. High-resolution XPS spectra of Al 2p (a) and Si 2p (b) in C600KT.

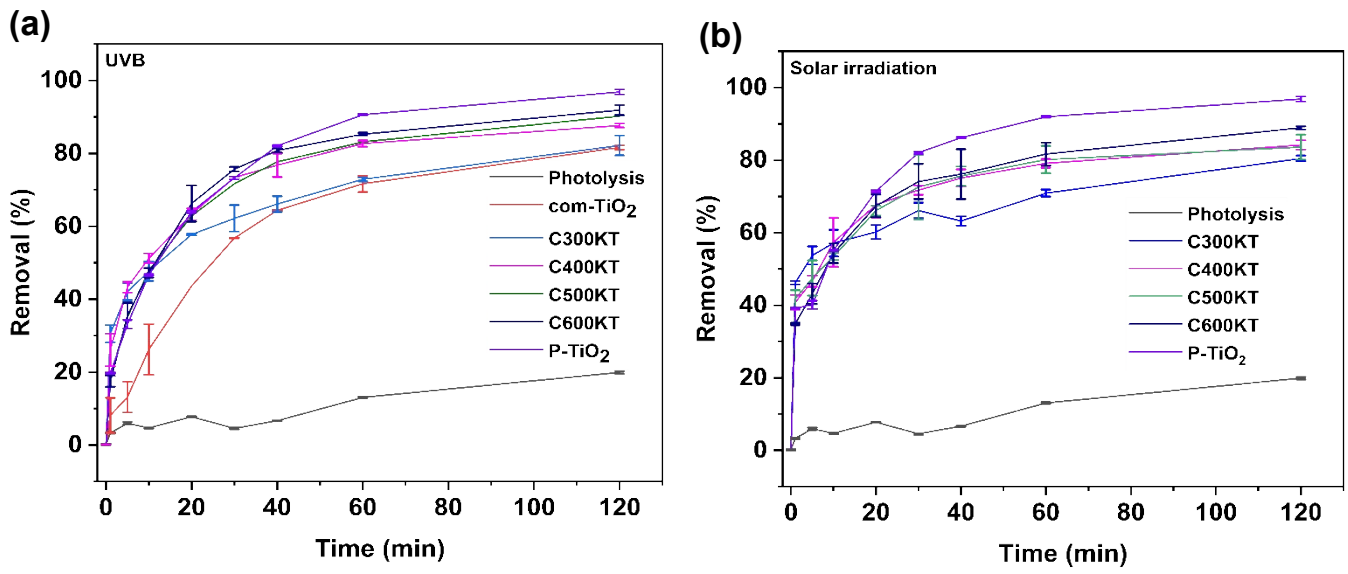
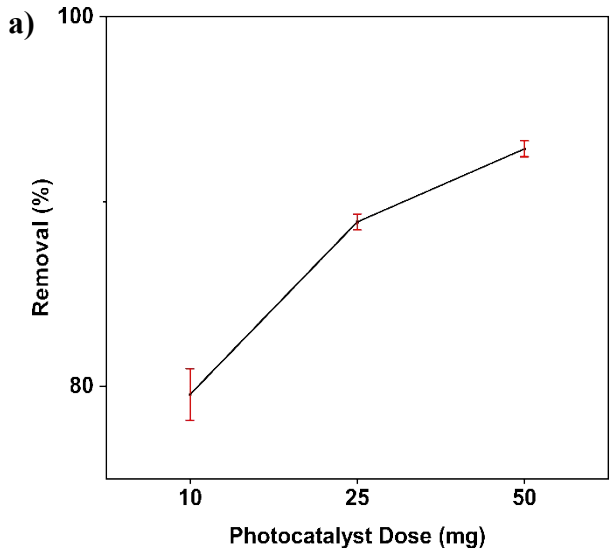
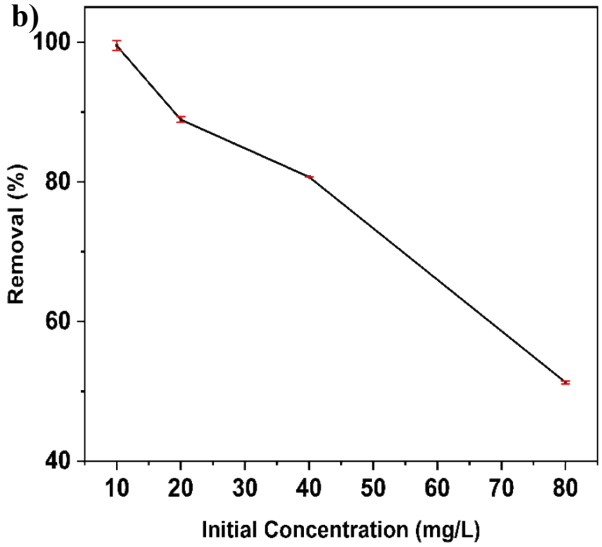
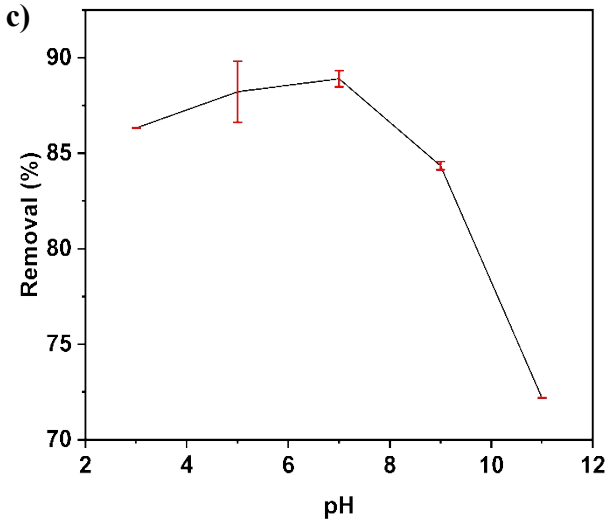
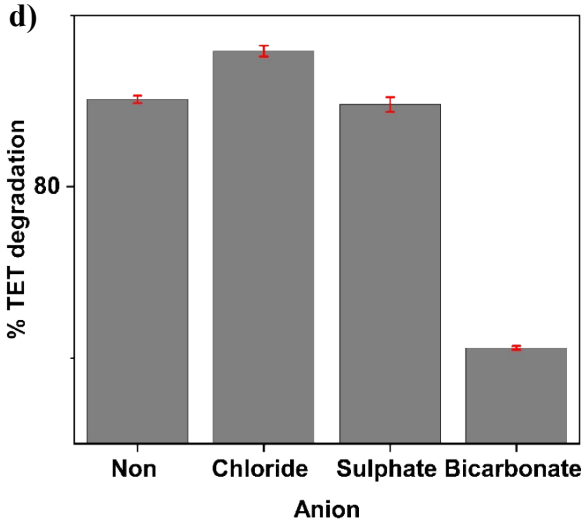


Figure S3. Degradation of TET under (a) UVB and (b) solar irradiation using com-TiO_2, P-TiO_2, C300KT, C400KT, C500KT, and C600KT along with the control photolysis experiment (no catalyst present). This figure is a replot of Figure 4 in the main manuscript to illustrate the small error bar for these experiments


a)
100
80
Removal (%)
10
25
50
Photocatalyst Dose (mg)


b)
100
80
60
40
Removal (%)
10
20
30
40
50
60
70
80
Initial Concentration (mg/L)


c)
90
85
80
75
70
Removal (%)
2
4
6
8
10
12
pH


d)
80
% TET degradation
Non
Chloride
Sulphate
Bicarbonate
Anion

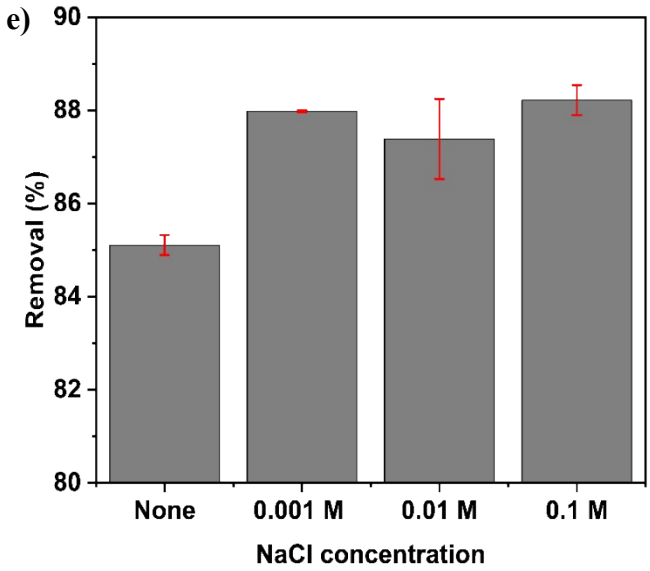

e)
90
88
86
84
82
80
Removal (%)
None
0.001 M
0.01 M
0.1 M
NaCl concentration

Figure S4. Effect of (a) photocatalyst dose, (b) initial concentration of TET at fixed catalyst dose, (c) initial TET solution pH, (d) anion species, and (e) ionic strength on the TET degradation efficiency of C600KT. This figure is a replot of Figure 5 in the main manuscript to illustrate the small error bar for these experiments.

Table S1: Comparison of TET degradation experiments (experimental conditions) and degradation efficiencies obtained in this study vs. data reported in the literature.

Material	Light source	Experimental condition	Degradation (%)	TOC removal (%)	Reference
Nanosized titanium dioxide, P25	Mercury lamps, 365 nm	I.C. = 40 mgL^{-1}, volume of solution = 40 mL, Mass =1000 mgL^{-1} , C.T. = 60 min	95	60	[1]
Commercial TiO_2-P25	300 W xenon lamp, 500 nm	I.C. = 10 mgL^{-1}, Volume of solution = 100 mL Mass= 20 mg , C.T.= 150 min	56.7	N/A	[2]
Pine cone derived C-doped TiO_2	Visible-LED light, 450 nm	I.C. = 5 mgL^{-1}, Volume of solution = 200 mL, Mass = 300 mgL^{-1} C.T. = 2 h	70	N/A	[3]
Black anatase-TiO_2	Xenon-lamp, >400 nm	I.C. = 10 mgL^{-1}, volume of solution = 100 mL, Mass,= 20 mg, C.T. = 240 min	66.2	29.6	[4]
TiO_2/activated carbon photocatalyst	Germicide UV lamp	I.C. = 50 mgL^{-1}, Volume = 0.2 g, Mass = 1.0 gL^{-1}, C.T. = 150 min	100	N/A	[5]
Orange peel biochar/clay/titania composites	UVB, 315 nm	I.C. = 20 mgL^{-1}, Volume of solution = 100 mL, Mass =	92	50	**This study**

		0.05 g, C.T. = 120 min			
Orange peel biochar/clay/titania composites	Natural sunlight	I.C. = 20 mgL^{-1}, Volume of solution = 100 mL, Mass = 0.05 g, C.T. = 120 min	89	60	**This study**

* Key: I.C. = initial TET concentration, C.T. = contact time, N/A = not available.

Figure S5. Comparison of 1 hour post-treatment recovery of pure titania (left) and titania hybrid clay nanocomposites (right)[6] These data clearly demonstrate that the composites are much easier to recover than pure titania particles. The latter do not sediment and are hard to separate from the liquid phase even via centrifugation.

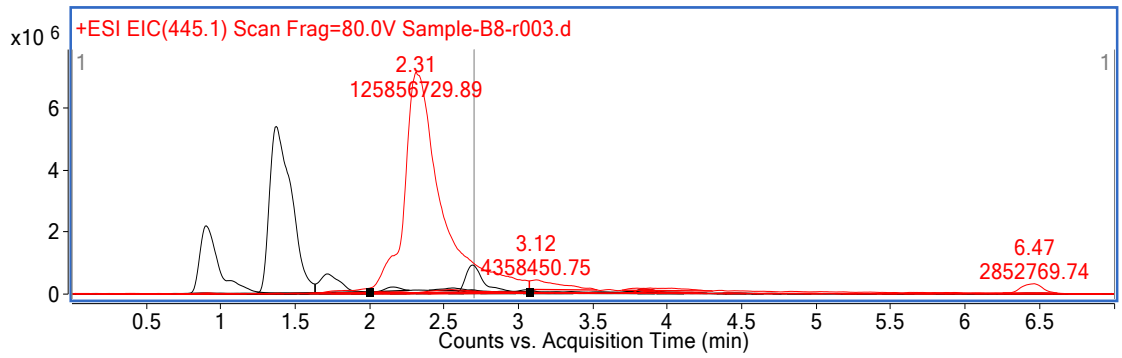


Figure S6. The extracted ion chromatogram of the LC-MS of the TET solution before (red) and after (black) degradation using C600KT. The major masses found are m/z 156, 170, 198 (breakdown products), and 441.5 (intact TET) as indicated in the following mass spectra in Figure S3-S5 at the corresponding retention times.

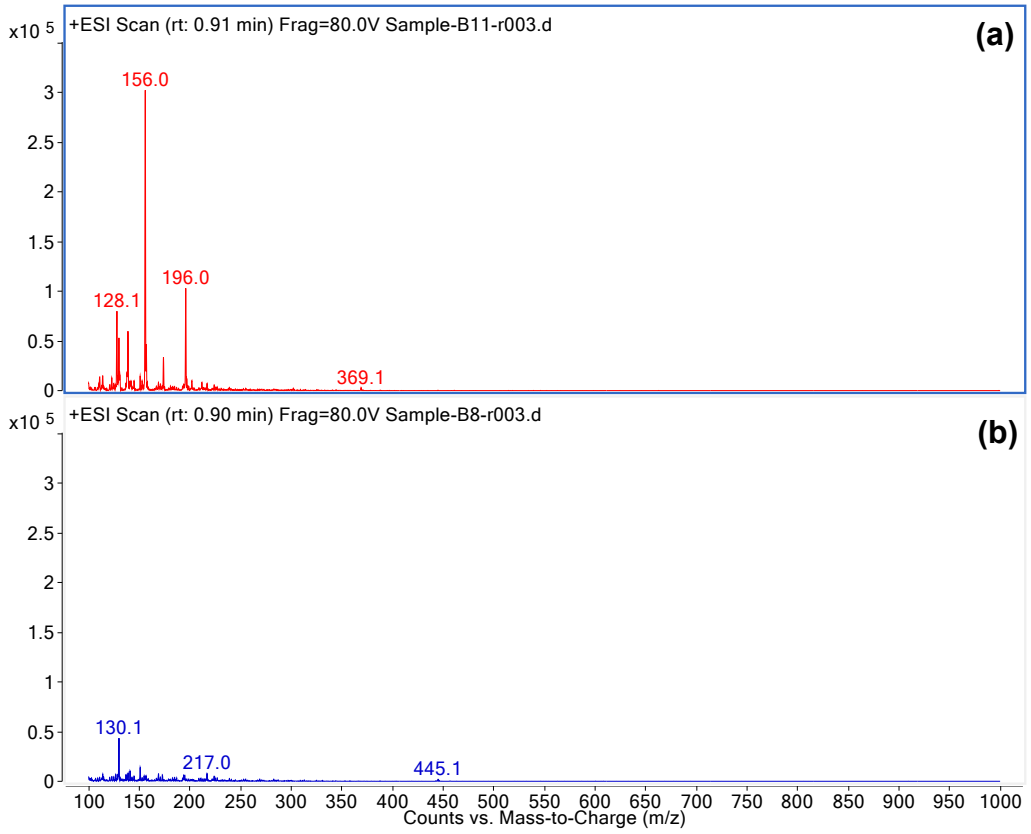


Figure S7. The extracted ion chromatogram of LC-MS of the intermediate products (a) and the control TET (b) at retention time 0.90 min. The curves above represent the treated (top) and the untreated TET (below) samples.

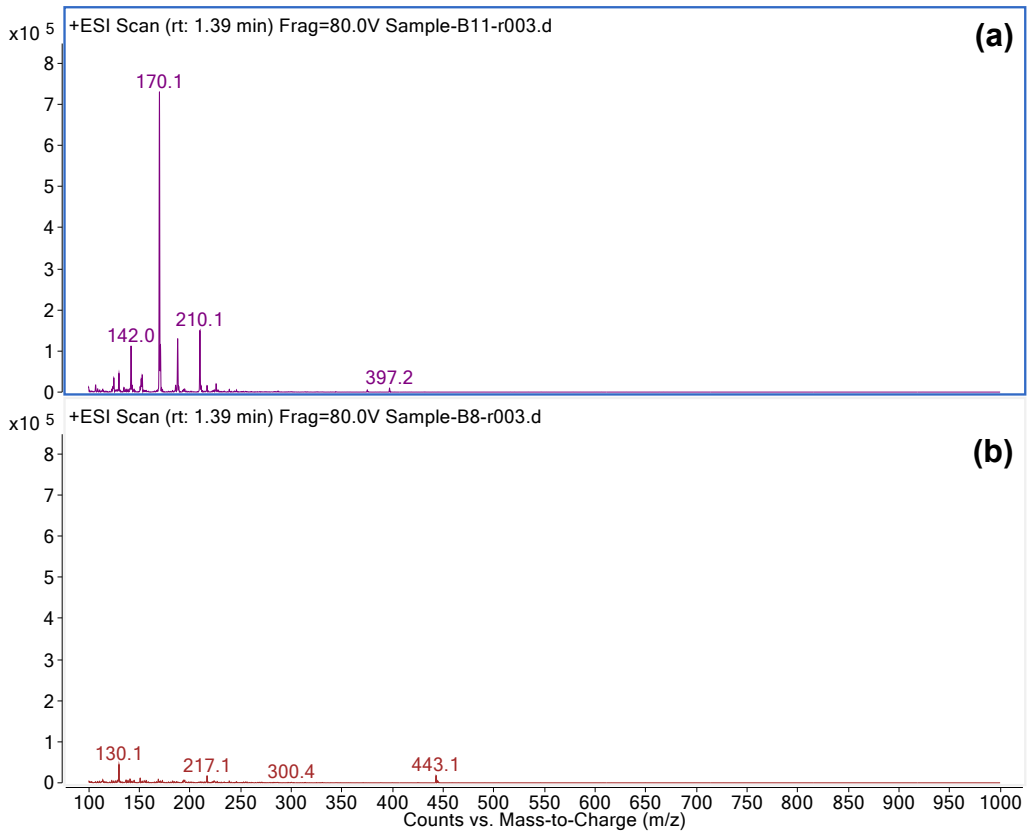


Figure S8. The extracted ion chromatogram of LC-MS of the intermediate product (a) and the control TET (b) at retention time 1.39 min. The curves above represent the treated (top) and the untreated TET (below) samples.

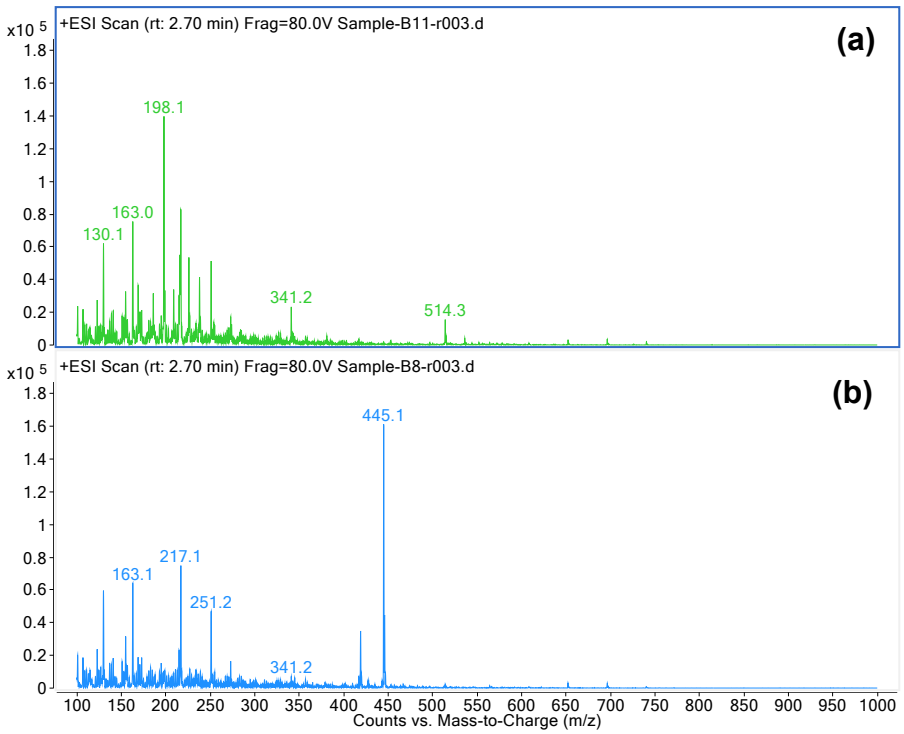


Figure S9 The extracted ion chromatogram of LC-MS of the intermediate product (a) and the control TET solution (b) at retention time 2.70 min. The curves above represent the treated (top) and the untreated TET (below) samples.

References

1. X.-D. Zhu, Y.-J. Wang, R.-J. Sun and D.-M. Zhou, Photocatalytic degradation of tetracycline in aqueous solution by nanosized TiO2, *Chemosphere*, 2013, **92**, 925-932.
2. S. Wu, H. Hu, Y. Lin, J. Zhang and Y. H. Hu, Visible light photocatalytic degradation of tetracycline over TiO2, *Chemical Engineering Journal*, 2020, **382**, 122842.
3. E. O. Oseghe and A. E. Ofomaja, Facile microwave synthesis of pine cone derived C-doped TiO2 for the photodegradation of tetracycline hydrochloride under visible-LED light, *Journal of environmental management*, 2018, **223**, 860-867.
4. S. Wu, X. Li, Y. Tian, Y. Lin and Y. H. Hu, Excellent photocatalytic degradation of tetracycline over black anatase-TiO2 under visible light, *Chemical Engineering Journal*, 2021, **406**, 126747.
5. A. C. Martins, A. L. Cazetta, O. Pezoti, J. R. Souza, T. Zhang, E. J. Pilau, T. Asefa and V. C. Almeida, Sol-gel synthesis of new TiO2/activated carbon photocatalyst and its application for degradation of tetracycline, *Ceramics International*, 2017, **43**, 4411-4418.
6. M. O. Adesina, I. Block, C. Günter, E. I. Unuabonah and A. Taubert, Efficient Removal of Tetracycline and Bisphenol A from Water with a New Hybrid Clay/TiO2 Composite, *ACS omega*, 2023, DOI: 10.1021/acsomega.3c00184.