Supplementary information

for

Ultrasonically modified alumina industry waste derived red mud beads coated with Z-scheme $Bi_{12}O_{15}Cl_6/Fe_2O_3$@C photocatalyst for enhanced degradation of antibiotics in wastewater

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Section S1 Analyte measurement technique

About 2 mL aliquots were collected from the outlet point, and filtered through a 0.22 μ polyvinylidene fluoride (PVDF) syringe filter for analysis. The concentrations of norfloxacin (NLX) and doxycycline (DCL) in the influent and effluent were measured using HPLC (Shimadzu, USA) equipped with a Shim-pack GWS C18 column (250 mm × 4.2 mm, 5 μm) and a UV-Vis diode array detector set at 278 nm,[1] and 350 nm.[2] The mobile phase comprised of water and acetonitrile in a proportion of 70:30 (V/V), with 0.1 % formic acid, having a flow rate of 1 mL/min. The temperature of the column was at 30 ^{o}C, and a 20 μL sample was injected each time.

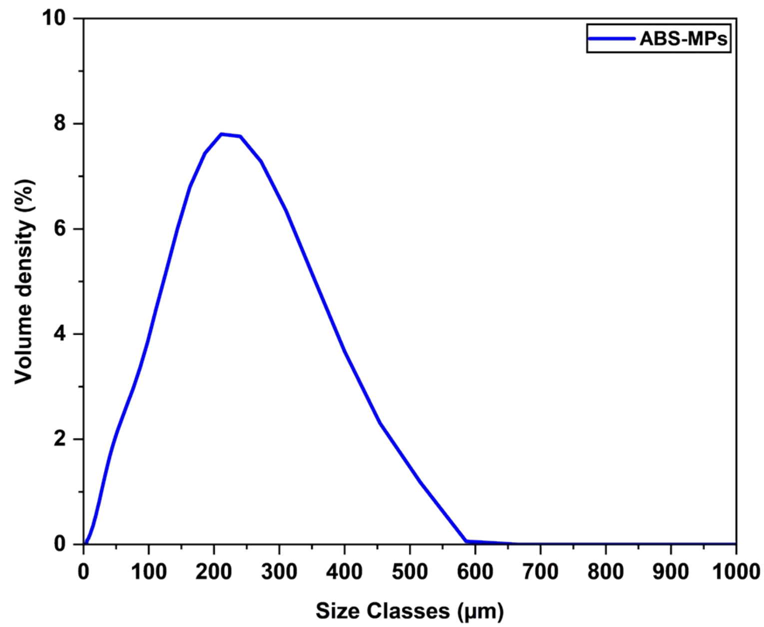


Fig. S1 Particle size distribution curve of acrylonitrile butadiene styrene micro-powder (ABS-MPs).

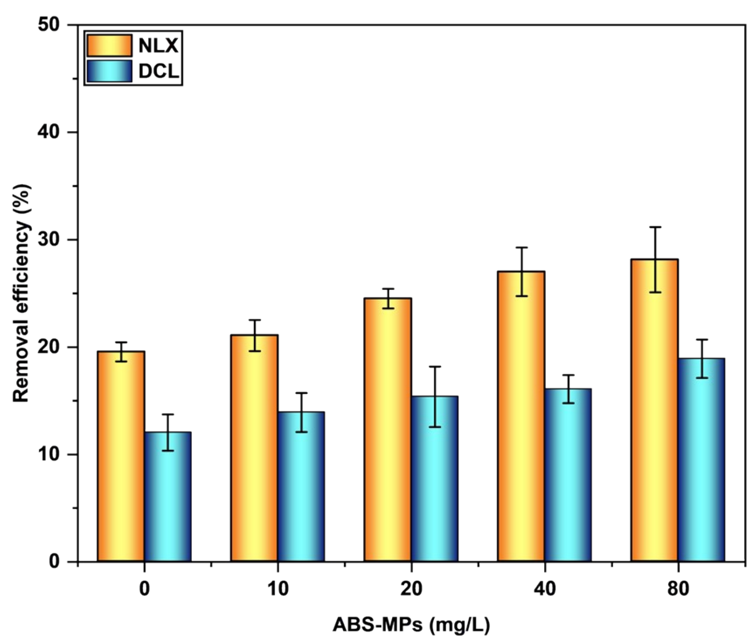


Fig. S2 NLX and DCL adsorption on BFC-II MRM beads in the presence of various concentrations of ABS-MPs.

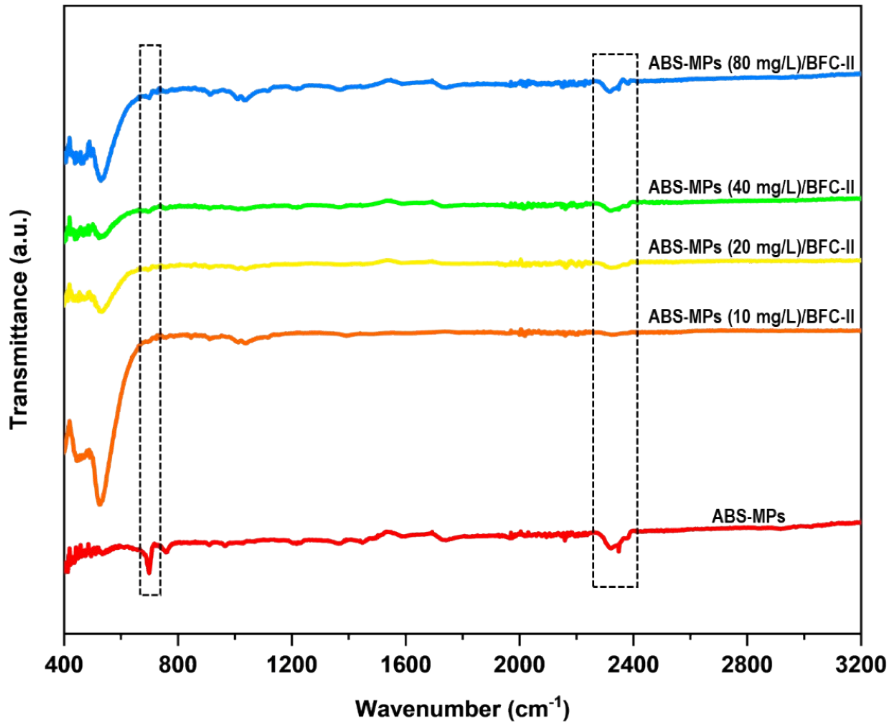


Fig. S3 FT-IR spectra of BFC-II coated MRM beads tested in the presence of various concentrations of ABS-MPs.

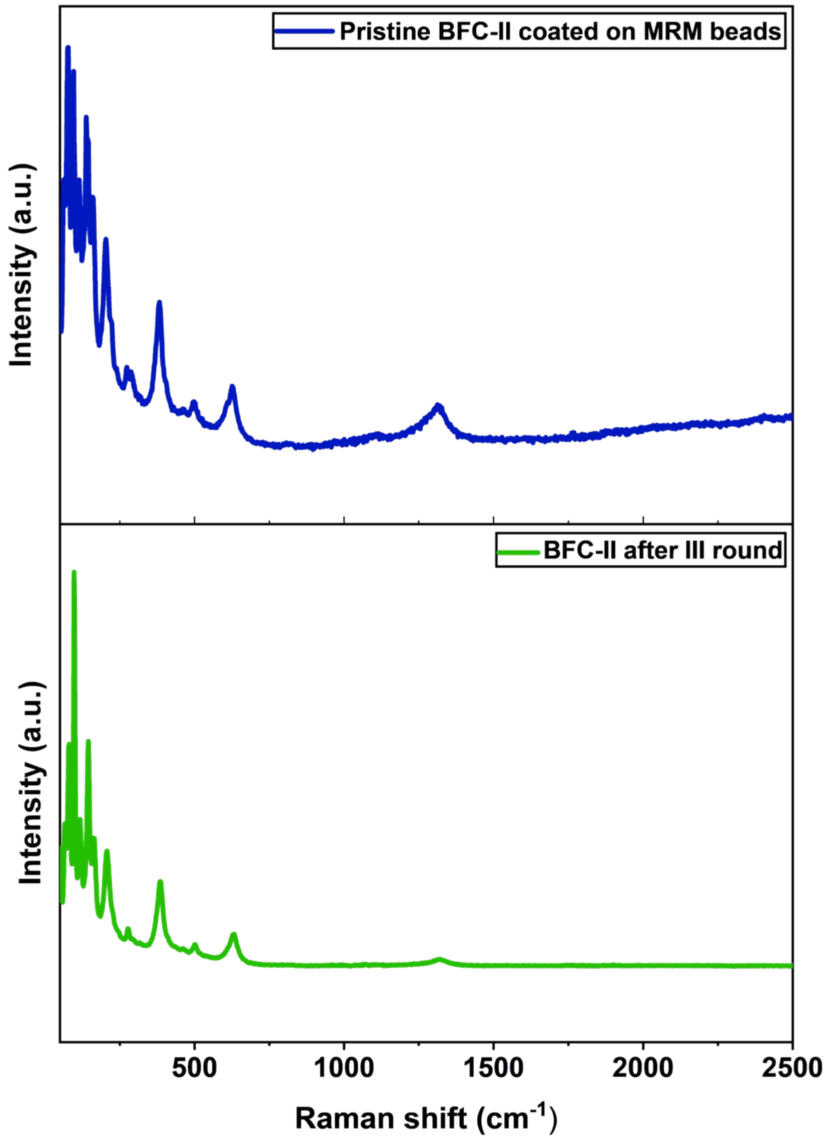


Fig. S4 Micro-Raman spectra of pristine BFC-II coated on MRM beads and BFC-II after third round (The peak at 1304 cm^{-1} confirms the presence of graphitic carbon (D band) in BFC-II, while the weaker peak at 1088 cm^{-1} suggests residual carbon formed during the combustion process).[3,4]

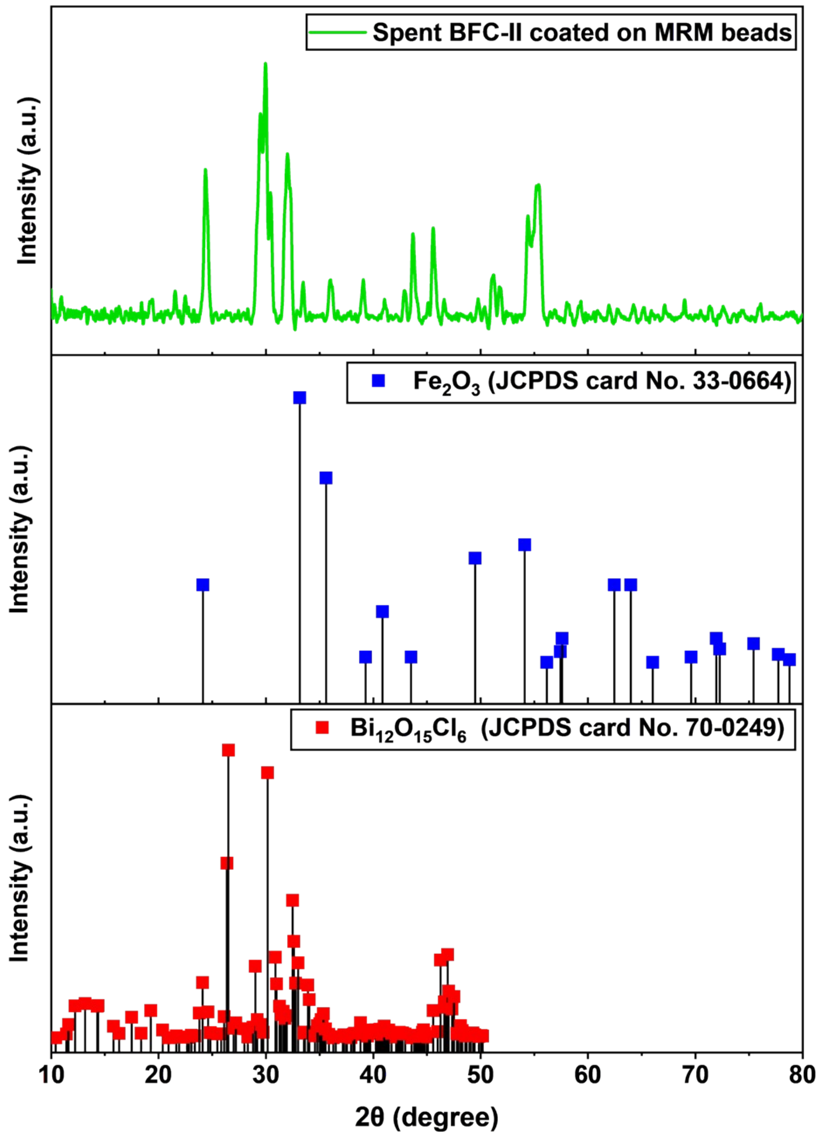


Fig. S5 XRD spectrum of the spent BFC-II coated MRM beads.

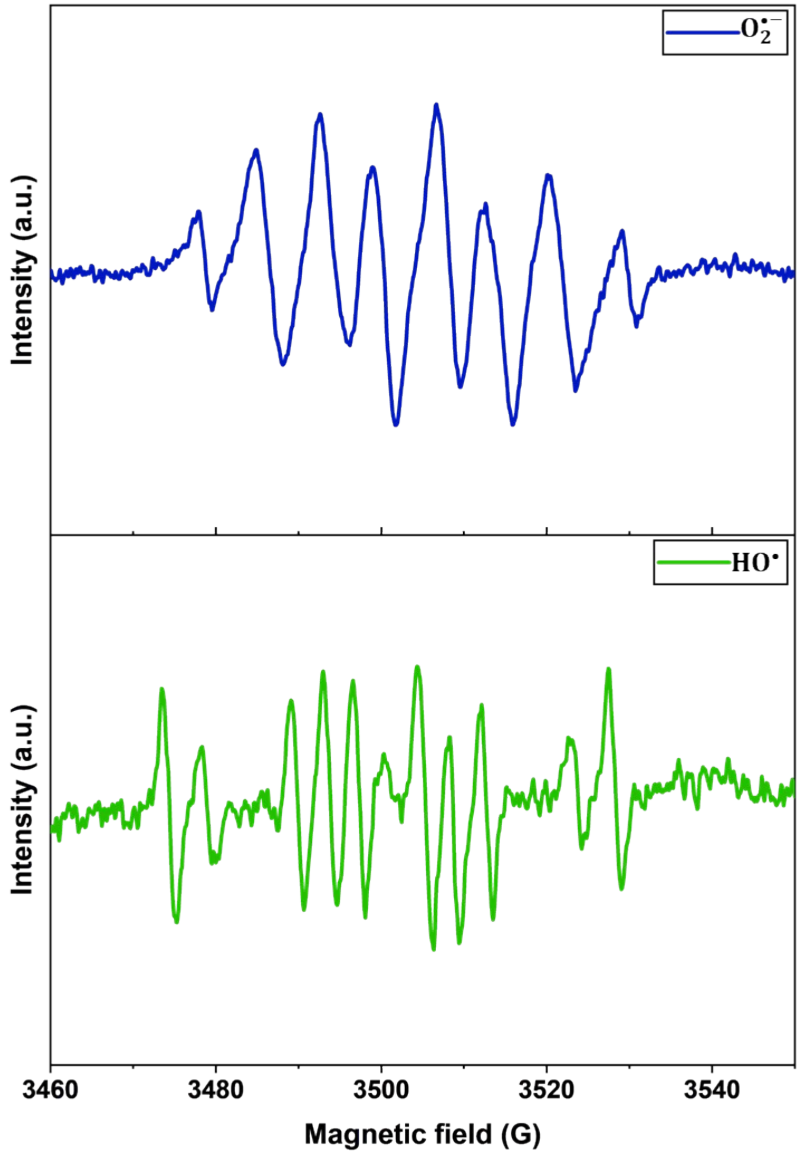


Fig. S6 Electron paramagnetic resonance (EPR) spectra for $O^{\bullet}{}_2^{-}$ and $HO^{\bullet}$ radicals.

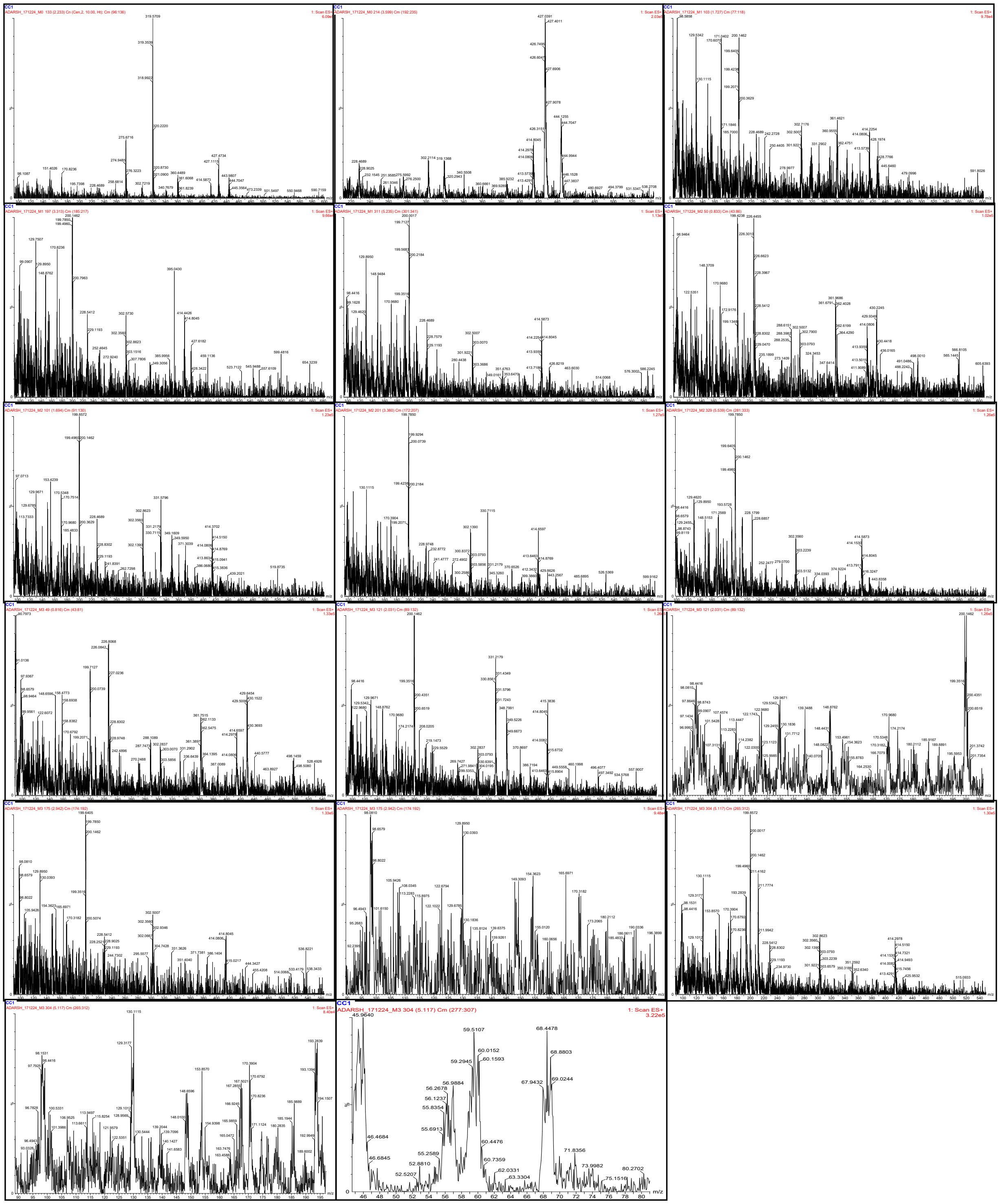


Fig. S7 LC-MS/MS chromatograms showcasing m/z corresponding to transformation products (TPs) of NLX and DCL (Along with influent (M0) and effluent (M3) samples, two intermediate samples were collected (M1 and M2)).

Table S1 Details of chemicals used in the present study.

S. No.	Name	Chemical formula	Purity	Company
1	Bismuth nitrate pentahydrate	$Bi(NO_3)_3 \cdot 5H_2O$	≥98%	Merck, India
2	Ferrous chloride hexahydrate	$FeCl_3 \cdot 6H_2O$	≥98%	Merck, India
3	Terephthalic acid	$C_8H_6O_4$	≥98%	Merck, India
4	N, N Dimethyl formamide	C_3H_7NO	≥99.8 %	Merck, India
5	Ethylene glycol	$C_2H_6O_2$	≥99.5 %	Merck, India
6	Ammonium chloride	NH_4Cl	≥99.5 %	Merck, India
7	Sodium nitrate	$NaNO_3$	≥99.0%	Merck, India
8	Sodium chloride	$NaCl$	≥99.0%	Merck, India
9	Sodium bicarbonate	$NaHCO_3$	≥99.7%	Merck, India
10	Sodium sulfate	Na_2SO_4	≥99.0%	Merck, India
11	Iron nitrate nano hydrate	$Fe(NO_3)_3.9H_2O$	≥98%	Merck, India
12	Aluminium nitrate nano hydrate	$Al(NO_3)_3.9H_2O$	≥98%	Merck, India
13	Sodium phosphate	Na_3PO_4	≥99.0%	Merck, India
14	Isopropanol	C_3H_8O	99.5%	Merck, India
15	Potassium iodide	KI	≥99.0%	Merck, India
16	Ascorbic acid	$C_6H_8O_6$	≥99%	Merck, India
17	Humic acid sodium salt	$C_9H_8Na_2O_4$	≥98%	Merck, India
18	Ethanol	C_2H_5OH	99%	SRL, India
19	Hydrochloric acid	HCl	37%	SRL, India
20	Sodium hydroxide pellets	NaOH	98%	SRL, India
21	Doxycycline	$C_{22}H_{24}N_2O_8$	HPLC grade, ≥98 %	Sigma-Aldrich
22	Norfloxacin	$C_{16}H_{18}FN_3O_3$	HPLC grade, ≥98 %	Sigma-Aldrich
23	Acrylonitrile Butadiene Styrene	$(C_8H_8 \cdot C_4H_6 \cdot C_3H_3N)_n$	≥99%	Nanochemazone

Table S2 Instrumentation techniques used in the present study.

S. No.	Instrument	Company
1	X-ray diffraction (XRD) analysis	D2 Phaser, Bruker, USA
2	X-ray fluorescence (XRF) spectrometer	Malvern Panalytical
3	Particle size analyzer	Malvern Panalytical
4	Micro-Raman spectroscopy	LabRAM HR Evolution, HORIBA Scientific
5	Fourier-transform infrared spectroscopy (FT-IR)	Bruker Alpha II
6	Field emission gun scanning electron microscopy (FEG-SEM)	Zeiss Merlin Gemini II, Germany
7	Atomic force microscopy (AFM)	Agilent 5500 Atomic Force Microscope
8	X-ray photoelectron spectroscopy (XPS)	PHI 5000 VersaProbe III, ULVAC PHI Inc., USA
9	Inductively coupled plasma mass spectrometry	iCAP Q, ICP-MS, Thermo Scientific, USA
10	Liquid chromatography-tandem mass spectrometry (LC-MS/MS)	Quattro microTM API, Waters, USA
11	Total organic carbon (TOC) analyzer	TOC-L Series, Shimadzu, Japan
12	High-Performance Liquid Chromatography (HPLC)	Shimadzu, USA

Table S3 Comparison of treatment performance of various immobilized photocatalysts reported in literature with the BFC-II coated MRM beads in a batch and continuous-flow photocatalytic reactor.

Photocatalyst	Immobilization means	Contaminant (Initial concentration)	Light source	Degradation efficiency (Residence time)	Reference
TiO_2	Hydrogel	Norfloxacin (3 mg/L)	UV lamp	13% (40 min)	[5]
F-Ti-SiO_2	Aerogel	Norfloxacin (10 mg/L)	UVC lamp	2.6305 mmol/h (Reaction rate)	[6]
SP-TiO_2	Carbon sponge	Sulfamethoxazole (10 mg/L)	LED light	80% (240 min)	[7]
g-C_3N_4	Stainless steel plates	Diclofenac (10 mg/L)	Xenon lamp	71% (240 min)	[8]
TiO_2-P25	Glass beads	Cefazolin (20 mg/L)	UV lamp	~100% (40 min)	[9]
S-doped Bi_2O_3/MnO_2	Clay beads	Acetaminophen, Sulfamethoxazole, and Iohexol (5 mg/L each)	LED light	87.1%, 82.6%, and 77.5% (300 min)	[10]
$Bi_{12}O_{15}Cl_6/Fe_2O_3$@C (BFC-II)	Ultrasonically modified red mud beads	Norfloxacin, and Doxycycline (5 mg/L each)	LED light	91.6%, and 82.6% (240 min)	**This work**

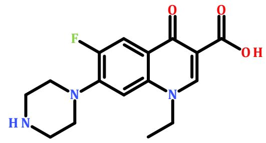
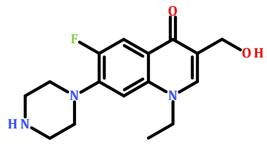
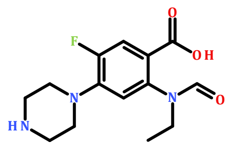
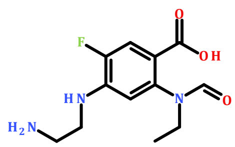
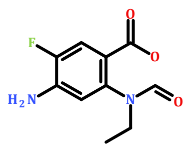
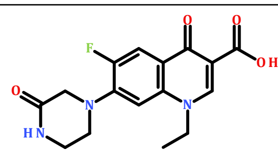
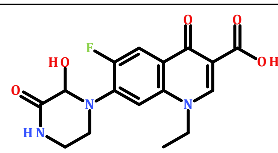
Table S4 Water quality parameters for real water matrices.

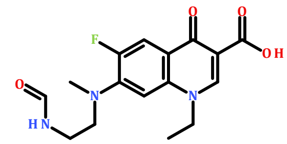
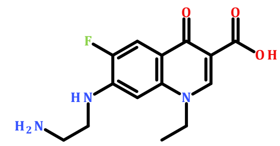
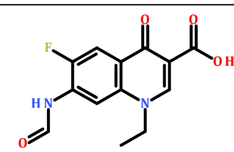
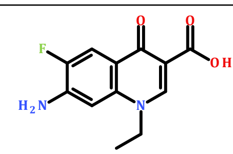
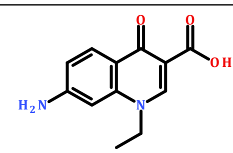
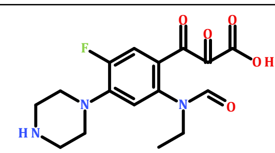
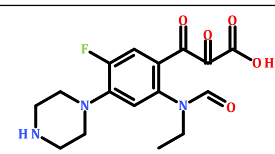
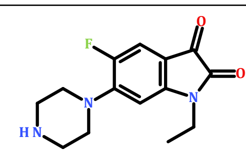
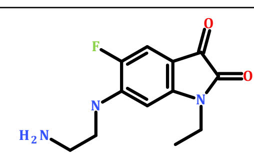
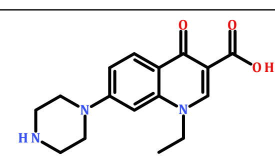
Parameters	DI water	Tap water	Surface water	Secondary wastewater
pH	6.8 ± 0.3	6.38 ± 0.2	6.52 ± 0.3	6.64 ± 0.5
Turbidity (NTU)	-	0.8 ± 0.3	9.4 ± 0.7	12.8 ± 1.5
TSS (mg/L)	-	-	48 ± 5	56 ± 3
TDS (mg/L)	-	92 ± 4	164 ± 2	337 ± 8
Chloride (Cl^-, mg/L)	0.34 ± 0.02	1.7 ± 0.4	14.8 ± 0.7	56.3 ± 3.1
Sulfate (SO_4^{2-}, mg/L)	0.51 ± 0.03	-	11.3 ± 1.9	19.8 ± 5.0
Nitrate (NO_3^-, mg/L)	-	-	22.5 ± 0.5	84.2 ± 0.3
Phosphate (PO_4^{3-}, mg/L)	-	-	4.70 ± 0.8	12.4 ± 0.5
COD (mg/L) [spiked with NLX: 5 mg/L and DCL: 5 mg/L]	-	-	81.4 ± 7	176 ± 4.5
NLX and DCL	5 mg/L each	5 mg/L each	5 mg/L each	5 mg/L each

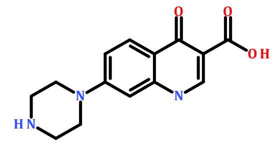
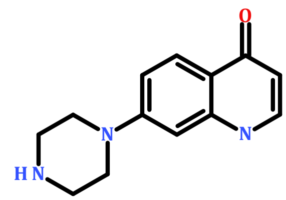
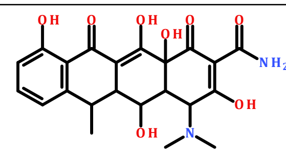
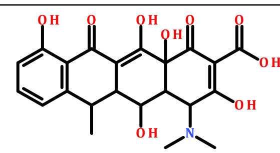
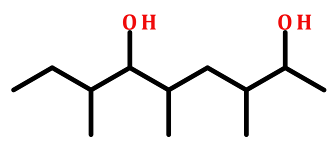
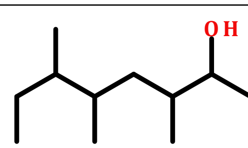
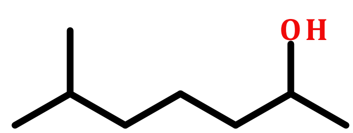
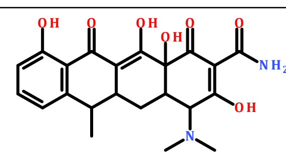
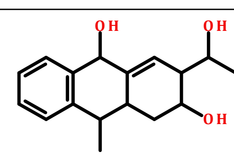
Table S5 Bi and Fe leaching in treated effluent quantified by ICP-MS.

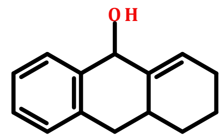
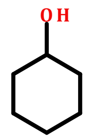
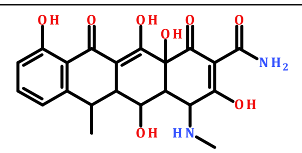
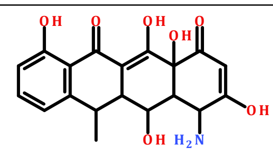
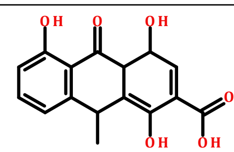
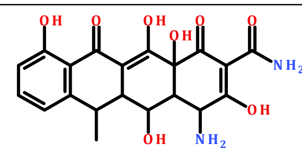
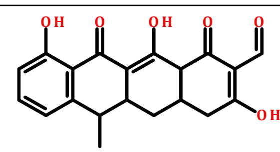
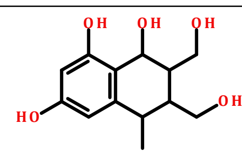
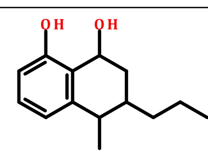
S. No.	Elements	Concentration (ppb)
1	Bi	0.7486
2	Fe	46.6607

Table S6 List of TPs of NLX and DCL identified through LC-MS/MS analysis (Source: **Fig. S7**).

Parent compounds/TPs	m/z	Chemical formula	Structure
NLX	319.57	$C_{16}H_{18}FN_3O_3$	
TP1	307.78	$C_{16}H_{20}FN_3O_2$	
TP2	295.56	$C_{14}H_{18}FN_3O_3$	
TP3	270.25	$C_{12}H_{16}FN_3O_3$	
TP4	227.02	$C_{10}H_{11}FN_2O_3$	
TP5	334.04	$C_{16}H_{16}FN_3O_4$	
TP6	350.31	$C_{16}H_{16}FN_3O_5$	

TP7	336.64	$C_{16}H_{18}FN_3O_4$	
TP8	295.55	$C_{14}H_{16}FN_3O_3$	
TP9	279.07	$C_{13}H_{11}FN_2O_4$	
TP10	250.44	$C_{12}H_{11}FN_2O_3$	
TP11	232.87	$C_{12}H_{12}N_2O_3$	
TP12	352.63	$C_{16}H_{18}FN_3O_5$	
TP13	324.34	$C_{15}H_{18}FN_3O_4$	
TP14	278.99	$C_{14}H_{16}FN_3O_2$	
TP15	252.46	$C_{12}H_{14}FN_3O_2$	
TP16	302.50	$C_{16}H_{19}N_3O_3$	

TP17	273.13	$C_{14}H_{15}N_3O_3$	
TP18	229.04	$C_{13}H_{15}N_3O$	
DCL	444.12	$C_{22}H_{24}N_2O_8$	
TP1’	445.64	$C_{22}H_{23}NO_9$	
TP2’	201.73	$C_{12}H_{26}O_2$	
TP3’	172.91	$C_{11}H_{24}O$	
TP4’	130.11	$C_8H_{18}O$	
TP5’	428.19	$C_{22}H_{24}N_2O_7$	
TP6’	273.13	$C_{17}H_{22}O_3$	

TP7’	200.14	$C_{14}H_{16}O$	
TP8’	99.09	$C_6H_{12}O$	
TP9’	430.22	$C_{21}H_{22}N_2O_8$	
TP10’	374.92	$C_{19}H_{19}NO_7$	
TP11’	303.00	$C_{16}H_{14}O_6$	
TP12’	416.32	$C_{20}H_{20}N_2O_8$	
TP13’	353.64	$C_{20}H_{18}O_6$	
TP14’	241.47	$C_{13}H_{18}O_5$	
TP15’	219.14	$C_{14}H_{20}O_2$	

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