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Supporting Information

Simultaneous removal of Acetaminophen, Sulfamethoxazole, and Iohexol from real wastewater in continuous mode by immobilized Sulfur-Doped Bi_2O_3/MnO_2 photocatalyst

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Chemicals and reagents

Acetaminophen (ACT, $C_8H_9NO_2$, 151.1 g mol^{-1}), sulfamethoxazole (SMX, $C_{10}H_{11}N_3O_3S$, 253.3 g mol^{-1}), and iohexol (IOX, $C_{19}H_{26}I_3N_3O_9$, M.W.: 821.1 g mol^{-1}) of HPLC grade (≥ 98% purity), and ciprofloxacin (CIF, $C_{17}H_{18}FN_3O_3$, 331.3 g mol^{-1}) (for toxicity experiments) were procured from Sigma-Aldrich. Humic acid ($C_9H_9NO_6$), sodium dihydrogen phosphate (NaH_2PO_4), sodium bicarbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), sodium chloride (NaCl), sodium nitrate ($NaNO_3$), magnesium chloride ($MgCl_2$), and calcium chloride ($CaCl_2$), were purchased from Merck, and SRL chemicals for carrying out the co-existing ions and natural organic matter effect experiments. Potassium dichromate solution ($K_2Cr_2O_7$), sulfuric acid (H_2SO_4), silver sulfate (Ag_2SO_4), and mercuric sulfate ($HgSO_4$) were procured from Sigma-Aldrich and were used for COD experiment. Ascorbic acid ($C_6H_8O_6$), isopropyl alcohol (C_3H_8O), Ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$), and sodium azide (NaN_3) were procured from Merck and SRL chemicals for performing radical scavenging experiments. All the chemicals used were of analytical grade (≥ 99% purity) and without further purification.

Analytical methods and characterization techniques

A reversed-phase ultra-high-performance liquid chromatography (UHPLC) system (Ultimate 3000, Thermo Fisher Inc., USA), equipped with a Hypersil GOLD (250 mm × 4.6 mm) C-18 column as stationary phase, was utilized to determine the residual concentration of ACT, SMX, and IOX in the reaction media. The instrument was operated in gradient mode with a binary mixture of acetonitrile and DI water as the mobile phase (30–65 vol.% acetonitrile), and the flow rate was 1 mL min^{-1}. A UV-vis diode array detector was used to detect ACT, SMX, and IOX at 254, 270, and 210 nm, respectively. Liquid chromatography-mass spectrometry (LC-MS) analysis (Waters 2695 XE - separations module equipped with Quattro Micro™ atmospheric pressure ionization (API) mass spectrometer, Waters

Corporation Inc., USA) was carried out to identify the intermediate compounds generated during photocatalytic degradation of ACT-SMX-IOX. The degree of mineralization of ACT, SMX, and IOX was measured using a total organic carbon (TOC) analyzer (TOC-L, Shimadzu Corporation, Japan). Ion chromatography (ICS 2100, Thermo Fisher Scientific Inc., USA) was used to determine the concentration of co-existing ions in the different water matrices tested in this study. The morphology, phase constitution, and surface chemistry of the spent catalyst were analyzed via microscopy and spectroscopy techniques. Fourier transform infrared (FTIR) spectroscopy was conducted using a Bruker Alpha II spectrometer provided by Bruker Corporation, USA. High-resolution field emission gun-scanning electron microscopy (FEG-SEM) was performed on a Zeiss Merlin field emission gun scanning electron microscope. The particle size distribution characteristics of the sand utilized in the FU were analyzed using a Zetasizer Nano ZS90 analyzer provided by Malvern PANalytical Ltd., Switzerland. The elemental composition of the sand grains before and after use as filtration media was approximated using X-ray fluorescence (XRF) spectroscopy (Epsilon 3, Malvern PANalytical Ltd., Switzerland). The concentration of metal ions leaching from the photocatalyst during the treatment process was estimated using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Optima 5300DV, Perkin Elmer, USA). In order to identify the primary reactive oxygen species (ROS) generated upon light exposure, electron paramagnetic resonance (EPR) spectroscopy was performed using an Elexsys 580 EPR spectrometer (Bruker Corporation, Germany).

Sampling and analysis

Real municipal and hospital wastewater samples were collected from the municipal treatment plant in situated in IIT Kharagpur campus, and a nearby sub-division hospital situated in Kharagpur, respectively. The samples were placed in approximately 20-liter containers, filled up to the brim, with no room for air, and subsequently stored in darkness at a temperature of

4°C. Samples were withdrawn from the inlet point of MBBR reactor (feed tank 1), intermediate settling tank (feed tank 2), and the MBBR-FU (feed tank 3) and analysed immediately following collection. The standard methods were employed to assess the physical and chemical attributes of the wastewater.[1] The COD of the wastewater samples was determined using the reflux colorimetric method using a COD digester. (5220 D[1]), and were measured at 420 nm (low COD) and 600 nm (high COD) using a UV-Vis Spectrophotometer (LabIndia 3092 Spectrophotometer, India). Total dissolved solids (TDS) the wastewater samples were calculated using a portable TDS meter. pH and turbidity were measured using pH meter and nephelometer respectively. TSS was measured by passing the sample through 0.45 μm glass microfiber filter paper and then heating the residue on the filter paper in an oven at 103–105 °C, following method 2540 D (APHA, 2017). Anions concentration in the wastewater samples were detected using ion chromatography (IC) (Thermo Fisher India, USA).

Synthesis of immobilized photocatalyst

In this study, 2S-BOMO coated clay beads (2S-BOMO CCB) has been used for ACT-SMX-IOX degradation. The detailed synthesis procedure for S-BOMO nanocomposite and immobilized photocatalysts are discussed in our previous study.[2]

Reactor setup and operation

Continuously-aerated MBBR-FU

In the MBBR unit the HDPE suspended carriers contributed to a design that promoted optimal surface area for biofilm attachment, and the system was supplemented with sufficient nutrients to enhance the efficiency of the wastewater treatment process. Before introducing real wastewater samples, the MBBR system underwent an essential acclimatization phase by inoculating tap water with activated sludge to make a synthetic wastewater system to

simulate real wastewater conditions (Fig. S2). The synthetic wastewater composed of glucose as carbon source (6900 mg L^{-1}) NH_4Cl (2700 mg L^{-1}), KH_2PO_4 (480 mg L^{-1}), $NaHCO_3$ (pH = 8.5 ± 0.3, to ensure sufficient alkalinity) as well as trace nutrients including, $MgSO_4.7H_2O$ (69.5 mg L^{-1}), $CaCl_2{\cdot}2H_2O$ (4.8 mg L^{-1}), $MnCl_2{\cdot}4H_2O$ (3.6 mg L^{-1}), $ZnSO_4{\cdot}7H_2O$ (5.7 mg L^{-1}), $FeCl_3{\cdot}6H_2O$ (18.9 mg L^{-1}), and $CuSO_4{\cdot}5H_2O$ (5.0 mg L^{-1}). In the synthetic wastewater, a chemical oxygen demand (COD) of 500 mg L^{-1}, NH_4^+-N of 50 mg L^{-1}, and a C/N ratio of 10 was maintained. During the entire acclimatization period, continuous monitoring of mixed liquor suspended solids (MLSS), organics, nutrients, and solids removal efficiency was performed. An MLSS concentration of 3500-4500 mg L^{-1} was maintained in the MBBR system. Once the removal efficiencies for the organics reached a steady level, it was assumed to be the end-point of the acclimatization period, signifying microbial adaptation to wastewater conditions. Aeration was supplied throughout the reactor at a rate of 5 L min^{-1} by an air pump to ensure continuous aerobic conditions within the system (Fig. S2).

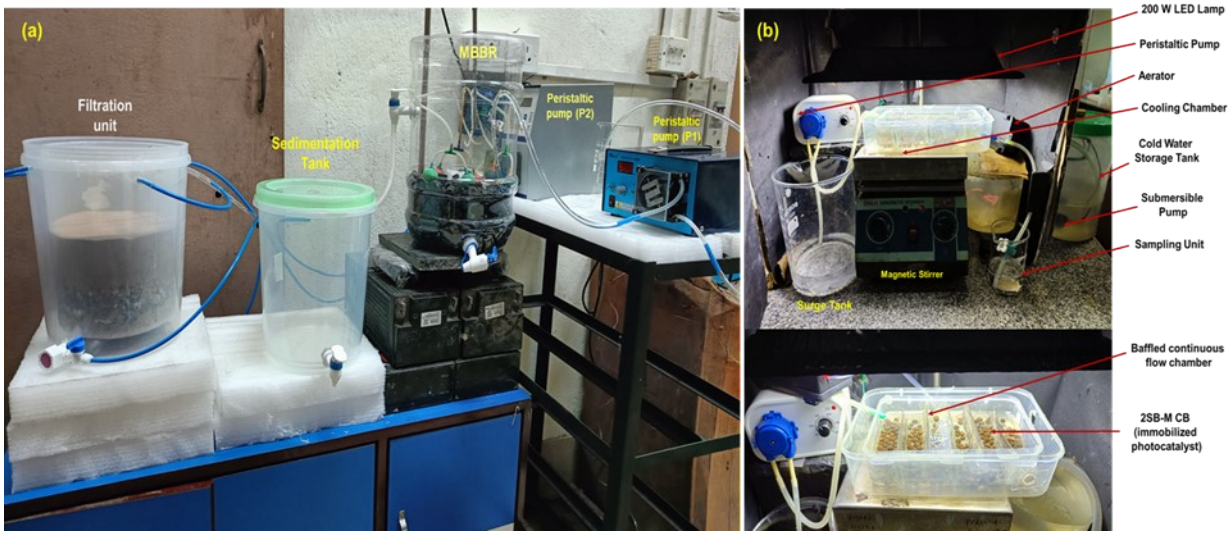


Fig. S1. (a) Image of MBBR unit followed by filtration unit. (b) Continuous photocatalytic reactor with immobilized photocatalysts (2S-BOMO CCB).

This aeration strategy was aimed at sustaining a dissolved oxygen (DO) level of approximately 4 to 6 mg L^{-1} and also to keep the carriers in suspension. The filtration unit

(FU) consisted of a fine sand layer (200-400 µm) of up to 9 cm (Fig. S3b), which was supported by gravel layers of varied size (2-4, 4-6 and 6-8 mm) (Fig. S3c). This multi-layered arrangement ensures efficient filtration, with each layer contributing to the removal of interfering agents.

Continuous photocatalytic reactor

To ensure adequate mixing and homogeneity of photocatalyst in the reaction chamber, diffused aerator system was applied in the reaction chamber, followed by slow magnetic stirring. Additionally, aeration may also enhance the dissolved oxygen concentration in the reaction solution, facilitating the generation of more reactive radicals that could further improve the photocatalytic process. The details regarding the light source used in this study are discussed in our previous study [3].

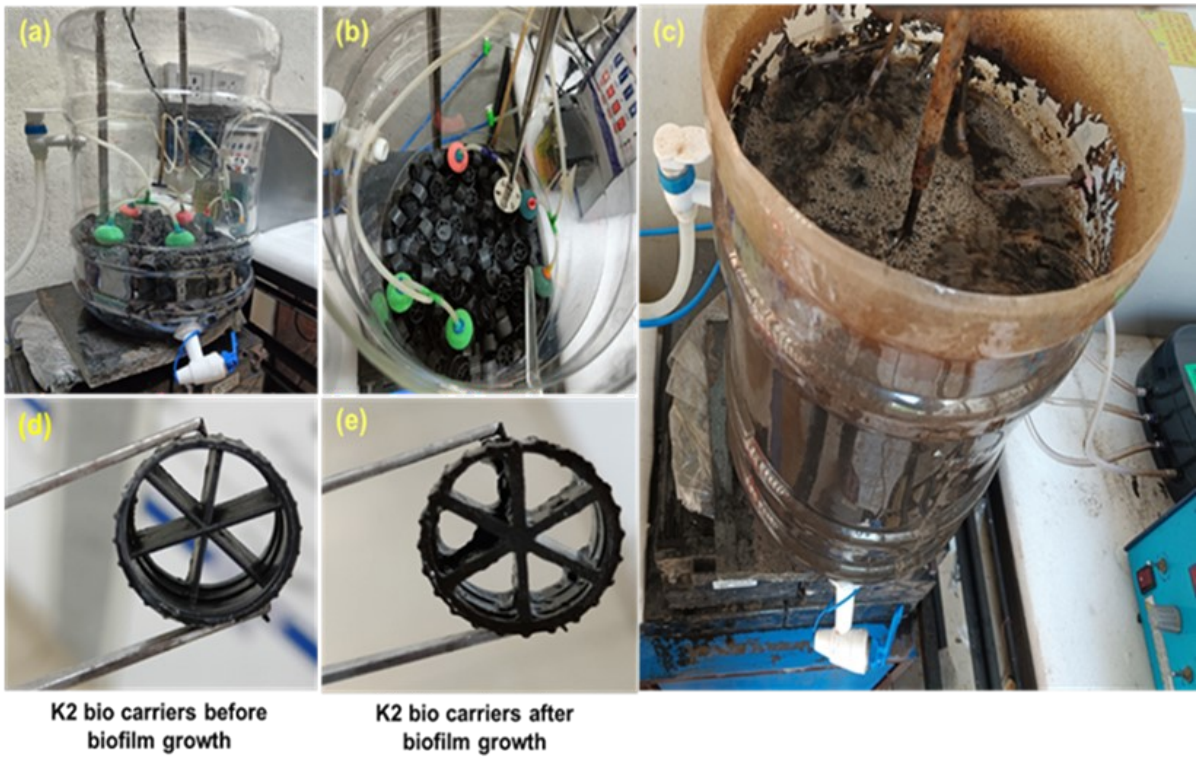


Fig. S2. (a) MBBR unit (K2 bio carriers (40% fil ratio)), (b) MBBR unit (aeration pipes). (c) MBBR system during acclimatization period. Kaldnes K2 bio carriers (c) before and (d) after the period of acclimatization.

Fig. S3. (a) Filtration unit (mesh shape water distribution), (b) siliceous sand (200-400 µm) used to fill the FU, and (c) coarse aggregates of varied size as support media for sand media.

Results and discussion

Synchronous photocatalytic degradation of ACT, SMX, and IOX in continuous mode

In a typical experiment, approximately 200 2S-BOMO CCB were placed in the baffled chamber and equally distributed over each baffled space to ensure a uniform packed-bed type chamber. After that, ~1 L of ACT-SMX-IOX solution (with a concentration of 5 mg L^{-1} each) was taken in the surge tank. The solution was then pumped into the reactor and allowed to interact with the photocatalyst in the dark for 60 min to achieve adsorption-desorption equilibrium. Thereafter, the system was irradiated for 240 min. The RT of 300 min (including the adsorption phase) was maintained in the rectangular chamber by adjusting the flow rate (~3.33 mL min^{-1}). After the irradiation period, aliquots were taken from the reactor, and the

residual concentration of each contaminant was analyzed, and the corresponding degradation rate constants were determined.

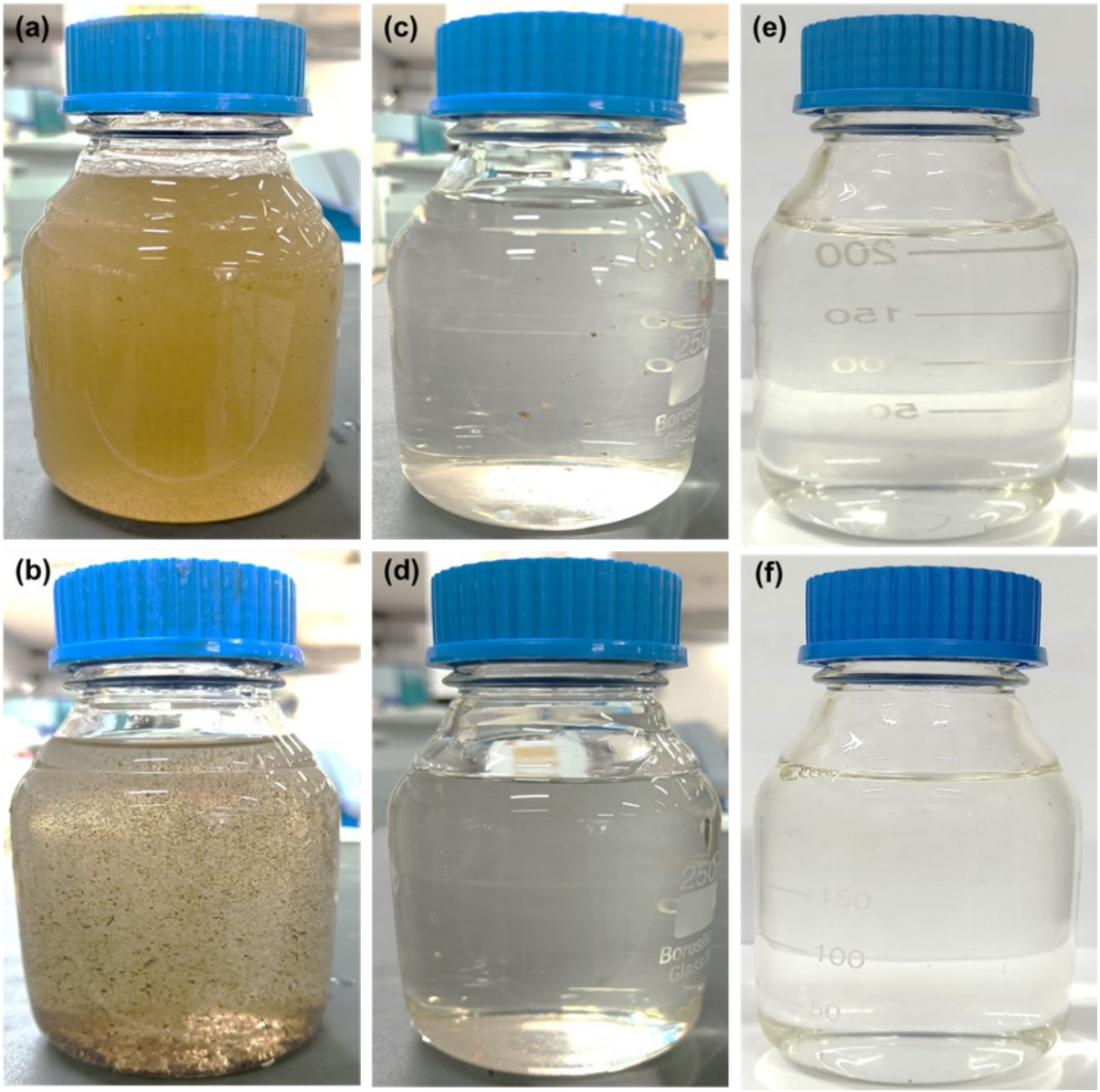
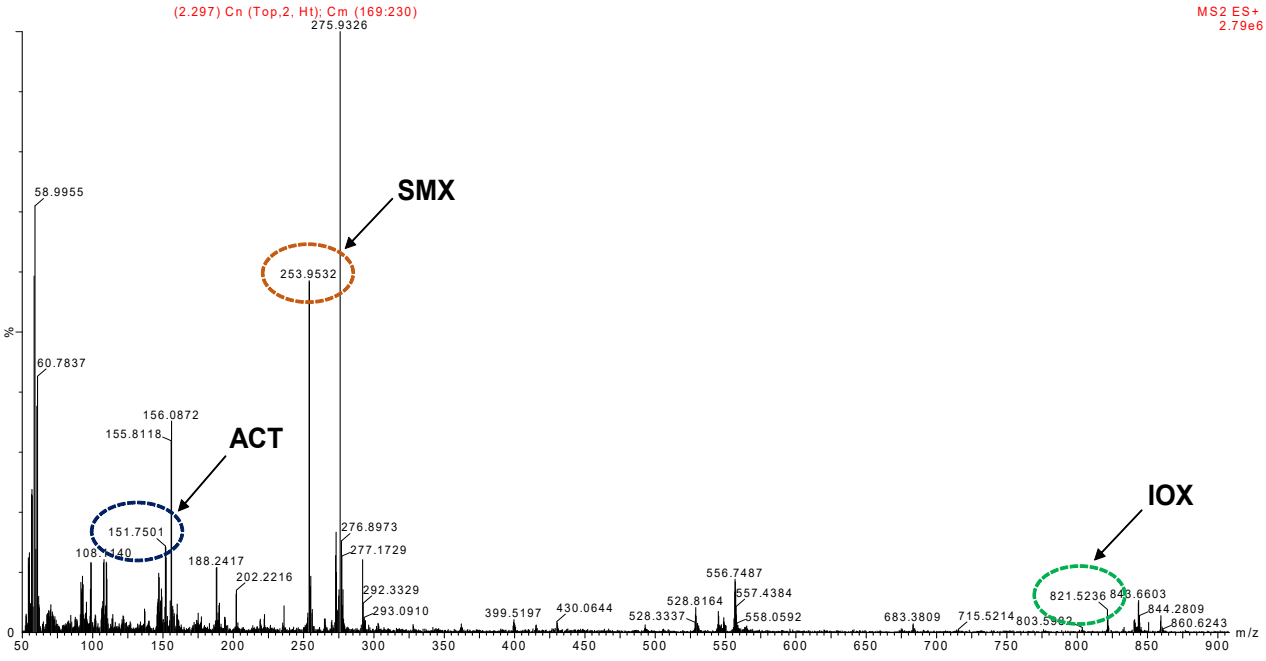


Fig. S5. Raw (a) MWW, and (b) HWW. MBBR treated (c) municipal wastewater, and (d) hospital wastewater. (e) MBBR-FU treated (e) municipal wastewater, and (f) hospital wastewater.

Table S1. Water quality parameters of real municipal and hospital wastewater used in this study.

Parameters	Raw municipal wastewater	Raw hospital wastewater
pH	6.96 ± 0.1	7.25 ± 0.1
Turbidity (NTU)	97.5 ± 1.8	70.3 ± 1.0
TSS (mg L^{-1})	161.2 ± 4.7	146.2 ± 12.3
TDS (mg L^{-1})	231.5 ± 24.1	347.7 ± 18.7
Chloride (Cl^-, mg L^{-1})	55.1 ± 5.8	70.6 ± 2.8
Bicarbonate (HCO_3^-, mg L^{-1})	387.8 ± 12.4	453.0 ± 36.7
Sulpahte (SO_4^{2-}, mg L^{-1})	17.8 ± 1.9	30.7 ± 5.7
Total Kjeldahl nitrogen (TKN, mg L^{-1})	47.4 ± 3.9	21.7 ± 1.1
Nitrate (NO_3^-, mg L^{-1})	4.7 ± 1.7	3.1 ± 1.3
Phosphate (PO_4^{3-}, mg L^{-1})	40.6 ± 1.8	48.5 ± 2.2
COD (mg L^{-1})	388.0 ± 20.0	310.0 ± 14.0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SMX
ACT
IOX
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253.9532
58.9955
60.7837
156.0872
155.8118
151.7501
188.2417
202.2216
276.8973
277.1729
292.3329
293.0910
399.5197
430.0644
528.3337
528.8164
556.7487
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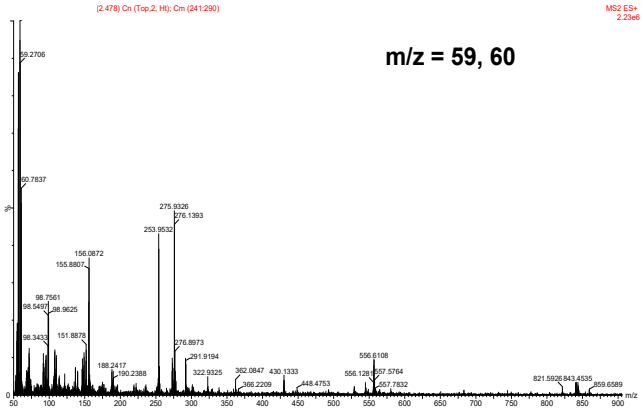
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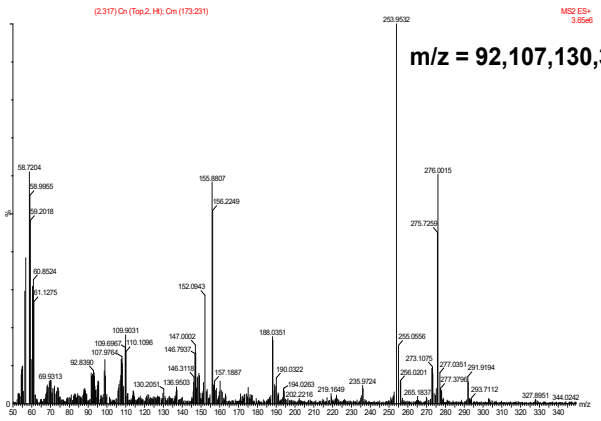
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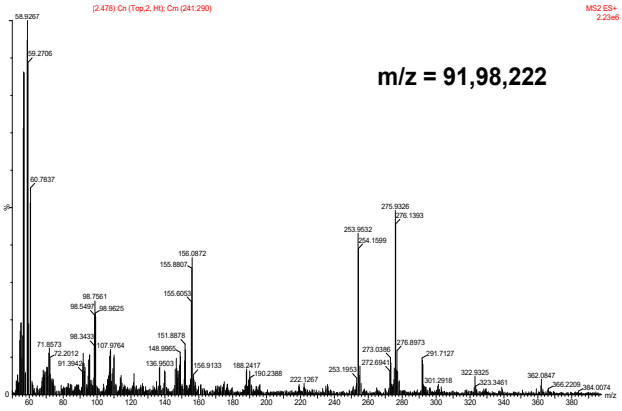
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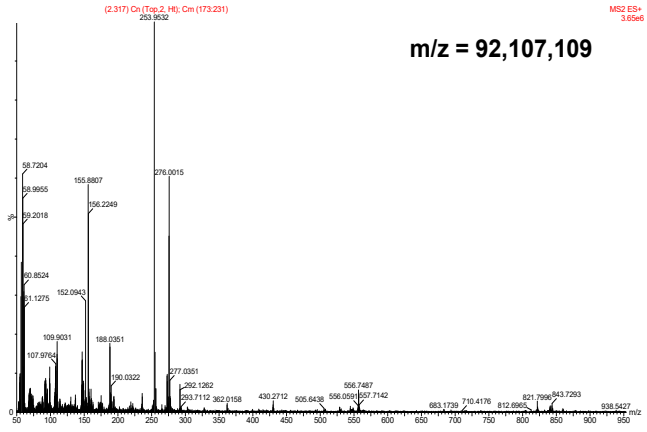
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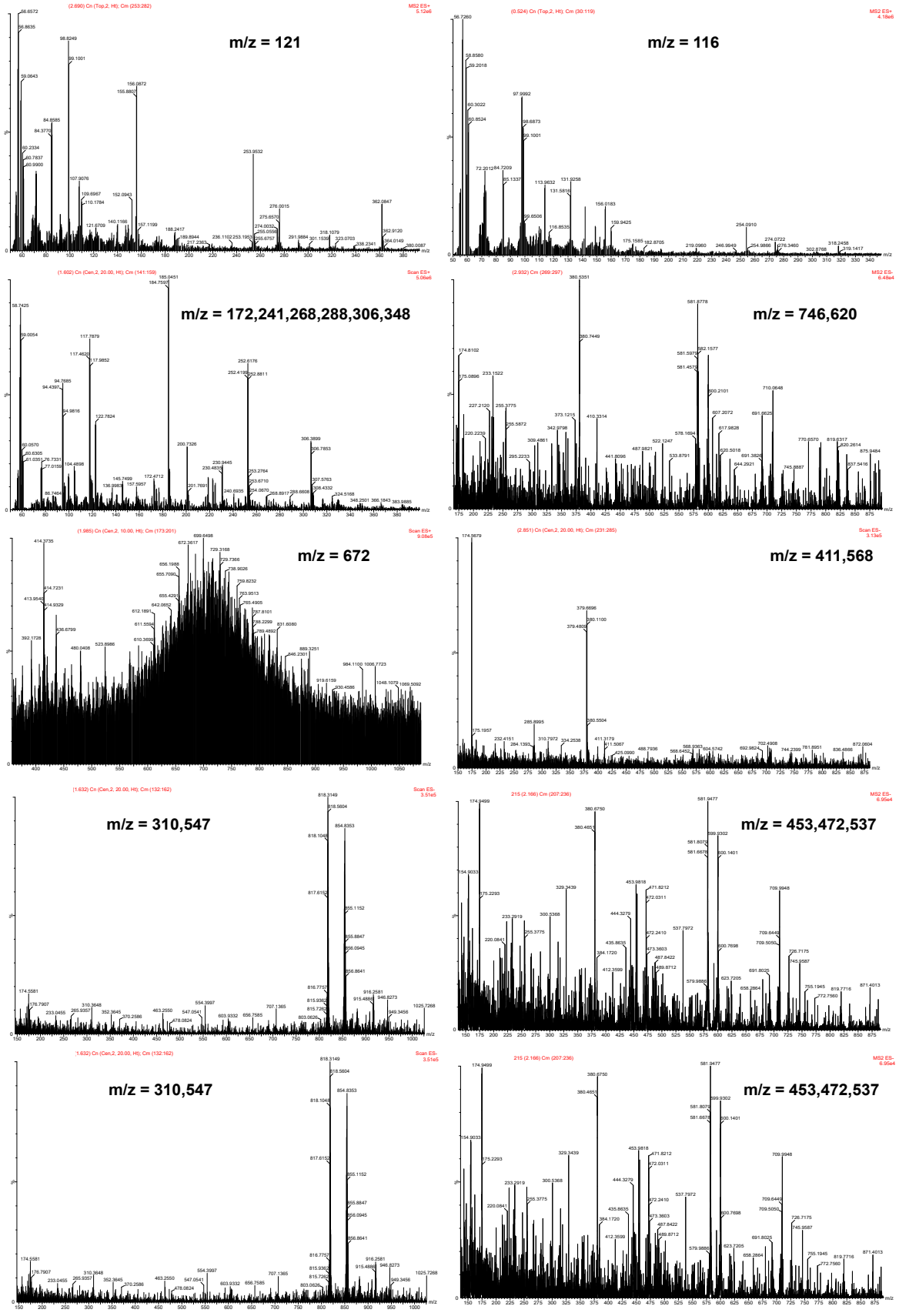

Fig. S6. LC-MS spectra of ACT-SMX-IOX intermediate by-products.

Table S2. Toxicity results predicted by T.E.S.T. software of the ACT, SMX and IOX and their intermediates.

Compound name	Molecular mass	Fathead LC_{50} (96 h) (mg L^{-1})	Daphnia LC_{50} (48 h) (mg L^{-1})	Oral rat LD_{50} (mg kg^{-1})	Developmental toxicity	Mutagenicity
ACT	151.1	89.69	27.14	1684.75	Non-toxicant (0.46)	Negative (0.45)
TPA5	122	25.2	38.82	3128.12	Non-toxicant (0.46)	Negative (0)
TPA6	116	462.48	410.27	828.18	Toxicant (0.72)	Negative (0.26)
TPA3	109	250.55	4.36	216.36	Toxicant (0.57)	Negative (0.44)
TPA1	108	31.96	63.64	-	Toxicant (0.61)	Negative (0.16)
TPA4	106	9.72	16.57	1393.53	Non-toxicant (0.24)	Negative (0.23)
TPA9	90	702.23	1445.45	1415.78	Toxicant (0.56)	Negative (0.3)
TPA10	89	578.76	308.54	1434.66	Toxicant (0.62)	Negative (0.2)
TPA11	73	368.37	44.98	333.87	Toxicant (0.54)	Negative (0.04)
TPA7	60	762.37	1035.97	3467.62	Toxicant (0.71)	Negative (-0.06)
TPA2	59	1092.96	353.09	1829.99	Toxicant (0.64)	Negative (-0.04)
TPA8	74	181.02	1491.62	945.75	Toxicant (0.58)	Positive (0.53)
SMX	253.27	-	-	8549.94	Toxicant (0.85)	Negative (-0.04)
TPS1	287	-	-	-	Toxicant (0.79)	-
TPS2	269	-	-	4851.33	Toxicant (0.8)	Negative (-0.14)
TSP3	241	-	-	N/A	Toxicant (0.91)	Negative (-0.2)
TSP4	197	-	-	-	Toxicant (0.71)	Negative (0.06)
TSP5	173	152.79	-	4269.24	Non-toxicant (0.45)	Negative (0.21)

TSP10	158	62.14	-	2474.44	Non-toxicant (0.49)	Negative (0.25)
TSP8	132	-	1242.62	N/A	Toxicant (0.54)	-
TSP6	109	75.33	3.34	406.69	Toxicant (0.57)	Negative (0.26)
TSP7	98	423.5	22.11	-	Non-toxicant (0.33)	Negative (0.39)
TSP9	93	80.87	2.97	372.73	Toxicant (0.53)	Negative (0.36)
IOX	821.1	0.6	-	-	Toxicant (0.75)	Negative (0.28)
TPI1	747	N/A	-	-	Toxicant (0.79)	-
TPI3	673	0.1	-	-	Toxicant (1.08)	-
TPI5	621	1.12	-	-	Toxicant (0.78)	-
TPI2	569	35.43	-	-	Toxicant (0.68)	Negative (0.27)
TPI4	547	0.41	-	-	Toxicant (1.07)	-
TPI8	537	14.09	-	-	Toxicant (0.7)	-
TPI10	453	33.84	-	-	Toxicant (0.88)	-
TPI9	411	34.18	2549.86	-	Toxicant (0.55)	Negative (0.05)
TPI6	347	18.04	-	-	Toxicant (1.05)	Negative (0.07)
TPI11	344	70.78	477.64	7650.5	Toxicant (0.67)	Negative (0.32)
TPI13	311	83.79	572.99	-	Toxicant (0.75)	Negative (0.31)
TPI7	305	21.92	-	-	Toxicant (0.93)	Negative (0.13)
TPI12	221	47.22	110.19	532.8	Toxicant (0.82)	Negative (0.32)

Degree of mineralization of ACT-SMX-IOX

The mineralization effieiciny of 2S-BOMO immobilized photocatalysts were mesurred by determining the reduction in the total organi carbon (TOC) of the ACT-SMX-IOX solution (5 mg L^{-1}). The TOC content was was reduced to 62.4% after 300 min of photocatalysis in contnous mode. The results can be explained by the fact that during photocatalytic degradation, the target pollutant produces a number of low molecular mass intermediates, dimers, and trimers that considerably increase the TOC content. Further, the higher residual TOC content suggests that ACT-SMX-IOX molecules are successfully mineralized to lower molar mass intermediate by-products and finally to H_2O and CO_2.

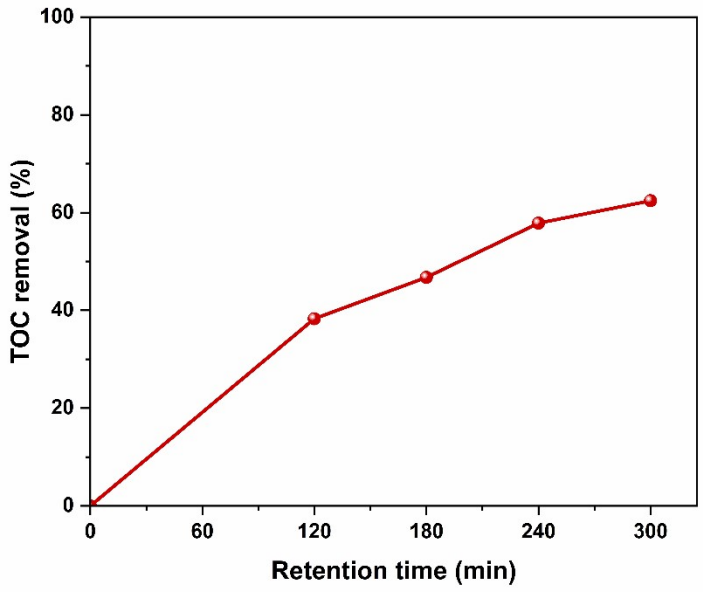

Fig. S7. TOC removal with respect to RT for simultaneous photocatalytic degradation of ACT, SMX, and IOX mixture over 2S-BOMO immobilized photocatalyst.

Cost and economics analysis

The reagents and chemicals used for the synthesis of immobilized photocatalyst for ACT-SMX-IOX degradation in the aqueous medium were purchased from Sisco Research Laboratories Pvt. Ltd., India, and Merck Millipore, India. To synthesize 2S-Bi_2O_3 and 2S-BOMO, we considered the cost of raw materials for preparing these substances in bulk. This approach reduces the overall cost of the materials, as the instrument cost remains constant regardless of whether the materials are prepared in bulk or in less quantity.

Table S3: Detailed cost analysis for the photocatalytic material synthesis and complete treatment process.

Instrument usage cost	**Power consumption (kW)**	**Operational time (h)**	**Cost ($) per kWh**	**Total cost ($)**
Sonicator	0.250	1	0.085	0.021
Muffle furnace (2S-Bi_2O_3)	3	4	0.085	1.020
Muffle furnace (Clay beads)	3	5	0.085	1.275
Hot air oven	1.500	10	0.085	1.275
Centrifuge	1	1	0.085	0.085
Magnetic stirring (2S-Bi_2O_3)	0.01	1	0.085	0.001
Magnetic stirring (2S-BOMO)	0.01	1	0.085	0.001
Chemicals acquired	**Quantity**	**Cost per quantity ($)**		**Total cost ($)**
For 2S-Bi_2O_3 (~60 g)				
Bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$)	65 g	38.4 per 500 g		4.99
Thiourea (CH_4N_2S)	0.31 g	7.4 per 500 g		0.004
Sodium hydroxide (NaOH)	20 g	3.7 per 500 g		0.148
Nitric acid (HNO_3)	75 mL	7.4 per 1000 mL		0.555
Total material cost incurred for 2S-Bi_2O_3 synthesis				5.697
Total instrument cost for 2S-Bi_2O_3 synthesis				2.130
Total cost incurred for 2S-Bi_2O_3 synthesis (~60 g)				7.827
For 2S-BOMO (~16 g)				
Potassium permanganate ($KMnO_4$)	15.8 g	8.3 per 500 g		0.262

Rochelle salt ($KNaC_4H_4O_6 \cdot 4H_2O$)	35 g	12.6 per 500 g	0.882
Sodium hydroxide (NaOH)	12 g	3.7 per 500 g	0.088
2S-Bi_2O_3	8 g	7.8 per 60 g	1.040
			2.272
Total instrument cost incurred for 2S-BOMO synthesis			1.230
Total cost incurred for 2S-BOMO synthesis (~16 g) (1:1 portion of 2S-Bi_2O_3 and MnO_2 were taken to prepared 2S-BOMO)			3.502
Total cost incurred for 2S-BOMO synthesis (1 g)			**0.218**
For clay beads (~1000 beads, 100 g mixture)			
Local clay	70 g	0.72 per 1000 g	0.050
Bentonite clay	20 g	5.4 per 1000 g	0.108
White cement	10 g	10.7 per 50000 g	0.002
			0.160
Total instrument cost incurred for preparing 2S-BOMO immobilized clay beads			2.260
Total cost incurred for preparing 2S-BOMO immobilized clay beads (~1000 nos.)			2.420
Total cost incurred for preparing 2S-BOMO immobilized clay beads (~200 nos.)			**0.484**

Capital Cost				
		Quantity	**Cost per quantity ($)**	**Total Cost ($)**
MBBR + Filtration unit	**Reactor fabrication cost**			
	Cost involved in the fabrication of the MBBR-FU unit with a working volume of ~14 L (MBBR) including piping and fittings			23.94
	Cost of the K2 carriers with 40% filling ratio	200 nos. (5.5L)	0.0075/nos	1.49
	Aerator cost	1	14.37	14.37
	Cost of raw material used			
	Gravel	2 kg	072/kg	1.44
	River sand	5 kg	0.036/kg	0.18
Photocatalytic reactor				
	Cost involved in the fabrication of the photocatalytic reactor with a working volume of 1 L including piping and fittings			11.97
	LED Light cost (200 W)	1	10.78	10.78
			Total capital cost ($)	**64.17**

Operational Cost

		Quantity	Power consumption (kW)	Operational time (h)	Cost ($) per kWh	Total cost $
MBBR + FU (Working volume: ~14 L)	Peristaltic pump (MBBR) (1 run)	1	0.05	8	0.085	0.034
	Peristaltic pump (FU) (1 run)	1	0.05	1	0.085	0.004
	Aeration pump (1 run)	1	0.005	8	0.085	0.003
Photocatalytic reactor (Working volume: 1 L)	Visible-light irradiation energy (14 runs)	1	0.2	14×4	0.085	0.952
	Aeration pump (14 runs)	1	0.005	14×5	0.085	0.030
	Peristaltic pump (14 runs)	1	0.005	14×5	0.085	0.030
	Submersible pump (14 runs)	1	0.0002	14×4	0.085	0.001
					Total operation cost ($)	**1.054**
			Treatment cost ($)/L with treatment of 14 L of wastewater			**0.076**

To prepare 2S-BOMO immobilized clay beads, roughly 1 g of the 2S-BOMO material is needed to coat approximately 200 immobilized clay beads (~6.45 mm diameter). These beads have the capacity to degrade approximately 1 L of ACT-SMX-IOX solution (5 mg L^{-1} of each) with a dose of 1 g L^{-1} of 2S-BOMO. It should be noted that performing experiments with immobilized photocatalysts is very convenient (i.e., recovery of the immobilized beads from reaction solution). Once the beads are placed in the photocatalytic reactor and these beads can be used for 5 to 6 photocatalytic runs continuously without much material loss.

References

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