

## Supporting Information

### Adsorption or photocatalysis?

#### **Engineering BiOI with metalorganic framework CAU-17 and microporous organic polymer MOP-CH2EDA to enhance ciprofloxacin removal from water**

Sepideh G. Khasevani<sup>a</sup>, Saulius Kaciulis<sup>b</sup>, Alessio Mezzi<sup>b</sup>, Shokat Sarmad<sup>c</sup>, Jyri-Pekka Mikkola<sup>c</sup>,  
Dariush Nikjoo<sup>a</sup>, Isabella Concina<sup>a</sup>

<sup>a</sup>Department of Engineering Sciences and Mathematics, Luleå University of Technology, 98187 Luleå,  
Sweden

<sup>b</sup>Institute for the Study of Nanostructured Materials, ISMN-CNR, 00015 Monterotondo  
Stazione, Roma, Italy

<sup>c</sup>Technical Chemistry, Department of Chemistry, Chemical-Biological Centre, Umeå University, SE-  
90871 Umeå, Sweden

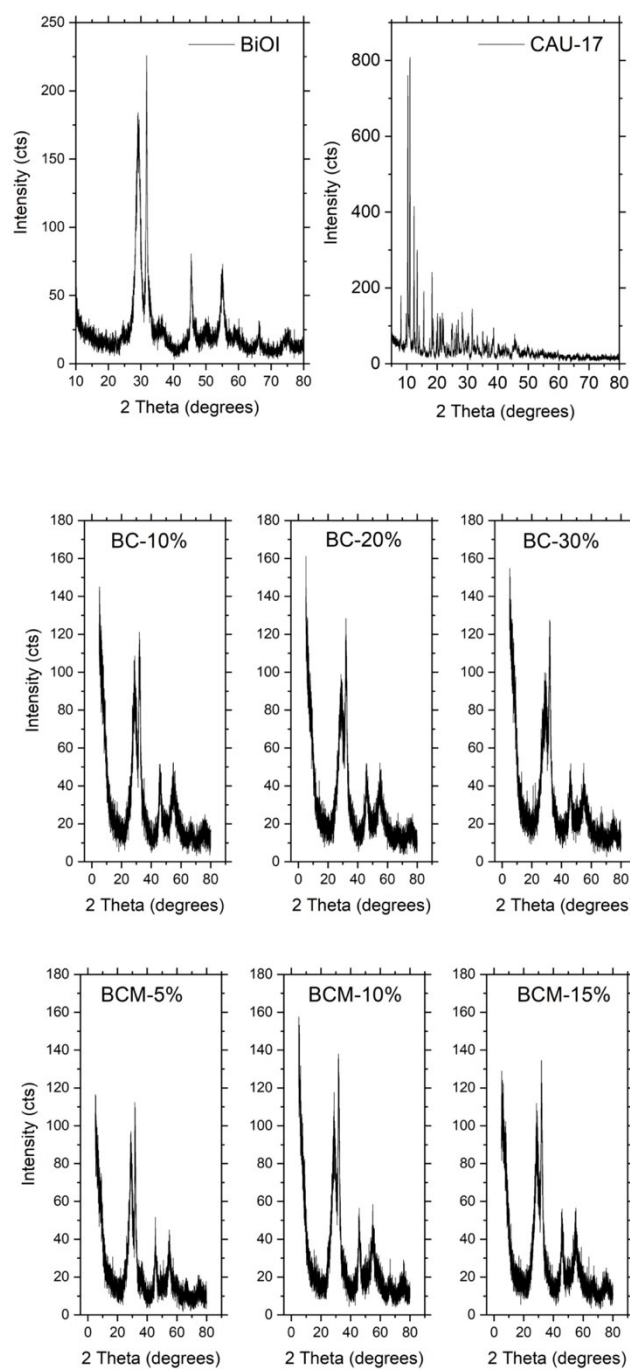


Figure S1. XRD patterns of the materials under investigation.

Prominent diffraction peaks of CAU-17:  $2\theta = 7.48^\circ, 9.947^\circ, 10.72^\circ, 11.23^\circ, 12.91^\circ, 13.3^\circ, 14.25^\circ, 16.99^\circ,$  and  $24.073^\circ$ . Main diffraction peaks of the tetragonal BiOI structure:  $2\theta = 29.64^\circ, 31.66^\circ, 45.67^\circ, 55.15^\circ,$  and  $65.1^\circ$  respectively [37].

Sample	BET surface area (m <sup>2</sup> /g)	Pore Volume average (mm <sup>3</sup> /g)	Pore Size average (nm)
BiOI	40.2	56	4.1
CAU-17	5.8	3.9	4.8
MOP-CH <sub>2</sub> EDA	684.2	640	5.1
BC-10%	55.7	97.6	5.4
BC-20%	54.7	95.1	5.4
BC-30%	35.9	79.8	6.3
BCM- 5%	24.9	46.4	6.1
BCM -10%	63.9	56	5.7
BCM-15%	48.7	83.5	5.5

Table S 1. Surface area and pore analysis of the prepared samples as retrieved from BET measurements.

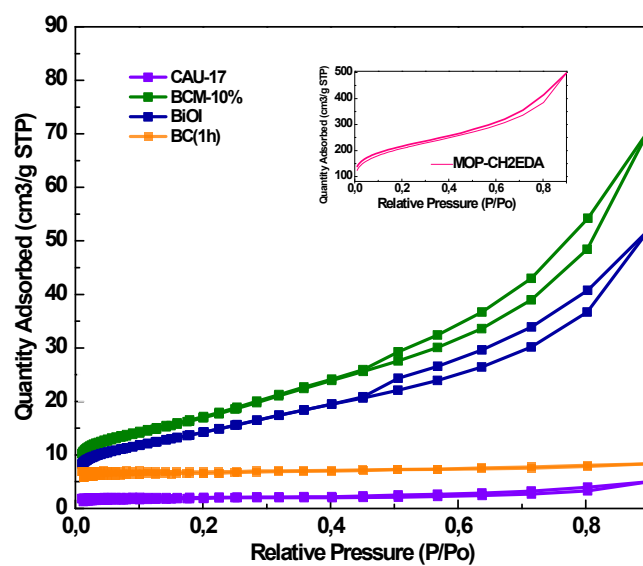


Figure S 2. Nitrogen adsorption-desorption isotherms for as-prepared materials.

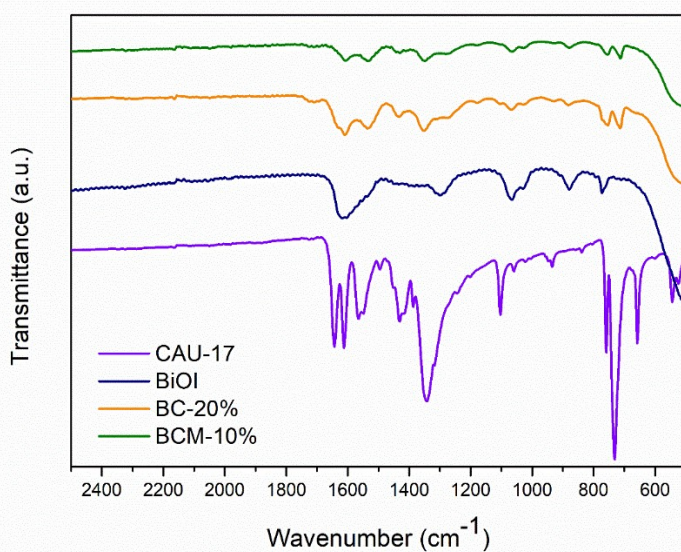


Figure S 3. FTIR spectra of the prepared materials.

Materials	Wavenumber (cm <sup>-1</sup> )	Vibration
BiOI	512	$\nu_{\text{sym}}$ Bi-O
	722	$\nu_{\text{asym}}$ Bi-O
	1385	$\nu$ Bi-I
	1650	$\delta$ O-H
	3450	$\nu$ O-H
CAU-17	400-800	O-Bi-O
	1100	$\nu$ C-H (benzene ring)
	1400	$\nu$ C-C (benzene ring)
	1373 and 1450	$\delta_{\text{sym}}$ and $\delta_{\text{asym}}$ COO <sup>-</sup>
	1550 and 1650	$\nu_{\text{sym}}$ and $\nu_{\text{asym}}$ COO <sup>-</sup>

Table S 2. IR correlation table.

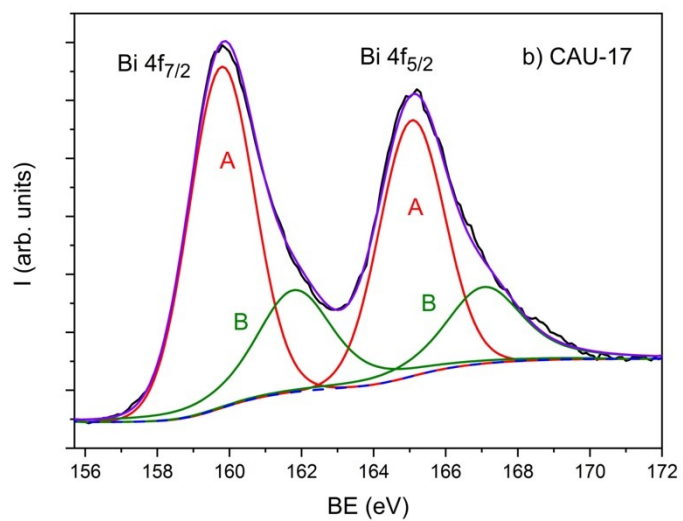
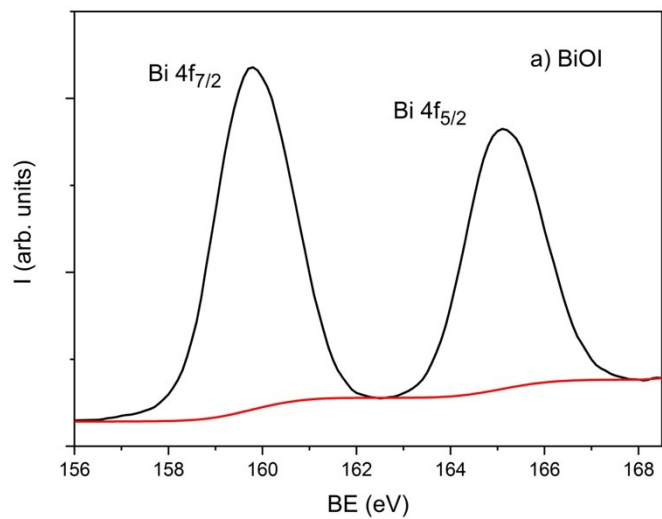
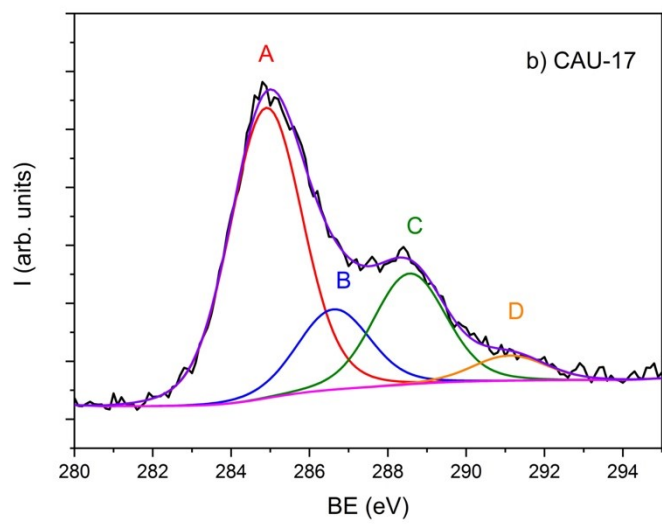
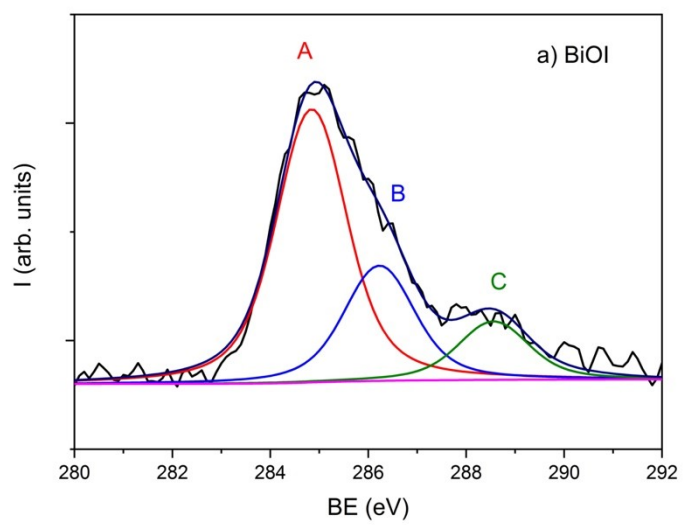


Figure S 4. Bi 4f photoemission spectra of the samples BiOI (a) and CAU-17 (b).



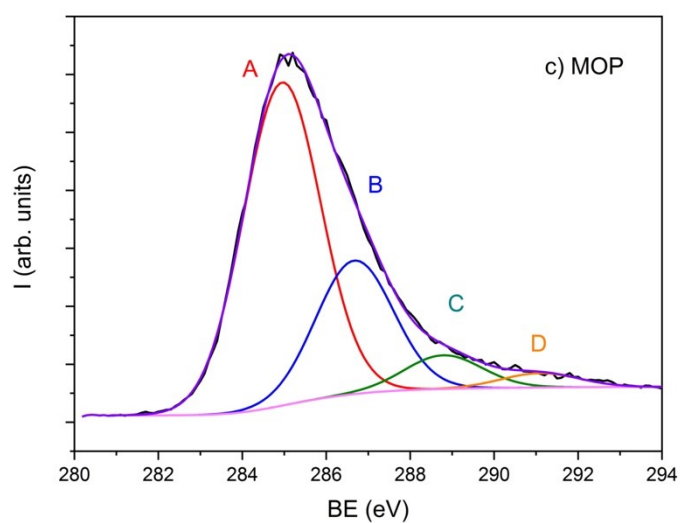


Figure S 5. C 1s photoemission spectra of the samples (a) BiOI, (b) CAU-17 and (c) MOP-CH2EDA.

Peak	BE (eV)	FWHM (eV)	Atomic %	State
Bi 4f <sub>7/2</sub>	160.0	1.9	23.4	Bi <sub>2</sub> O <sub>3</sub> , BiI <sub>3</sub>
C 1s - A	285.0	1.7	22.1	aliphatic
C 1s - B	286.4	1.7	9.4	C-O
C 1s - C	288.7	1.7	4.8	-C=O
I 3d <sub>5/2</sub>	619.2	1.7	13.9	iodide
O 1s - A	530.3	1.8	13.3	oxides
O 1s - B	531.9	1.8	10.1	OH <sup>-</sup> , C-O
O 1s - C	533.3	1.8	2.7	-C=O

Table S 3. XPS quantification tables with chemical state of the species for the samples BiOI

Peak	BE (eV)	FWHM (eV)	Atomic %	State
Bi 4f <sub>7/2</sub> - A	159.8	2.2	5.6	Bi <sub>2</sub> O <sub>3</sub>
Bi 4f <sub>7/2</sub> - B	161.8	2.5	2.3	Bi-O-C as in Bi

				acetate, see ref. [x]
C 1s - A	285.0	2.2	36.2	aliphatic
C 1s - B	286.6	2.2	10.0	C-O
C 1s - C	288.6	2.2	13.8	-C=O
C 1s - D	291.1	2.2	3.1	carbonate
N 1s	401.0	3.3	2.2	C-N, C-N-H
O 1s - A	531.0	2.2	22.1	oxides
O 1s - B	532.8	2.2	4.6	-C=O

Table S 4. XPS quantification tables with chemical state of the species for the sample CAU-17.

Peak	BE (eV)	FWHM (eV)	Atomic %	State
C 1s - A	285.0	2.2	55.3	aliphatic
C 1s - B	286.7	2.2	22.8	C-O
C 1s - C	288.8	2.2	5.8	-C=O
C 1s - D	291.1	2.2	2.4	carbonate
Cl 2p <sub>3/2</sub>	201.0	3.0	0.6	Cl <sup>-</sup>
N 1s - A	399.4	2.9	3.9	C-N, NH <sub>2</sub>
O 1s - A	532.4	2.7	6.7	OH <sup>-</sup> , -C=O
O 1s - B	534.0	2.7	2.0	-C-O
P 2p <sub>3/2</sub>	133.4	3.0	0.4	phosphate

Table S 5. XPS quantification tables with chemical state of the species for the sample MOP-CH2EDA.

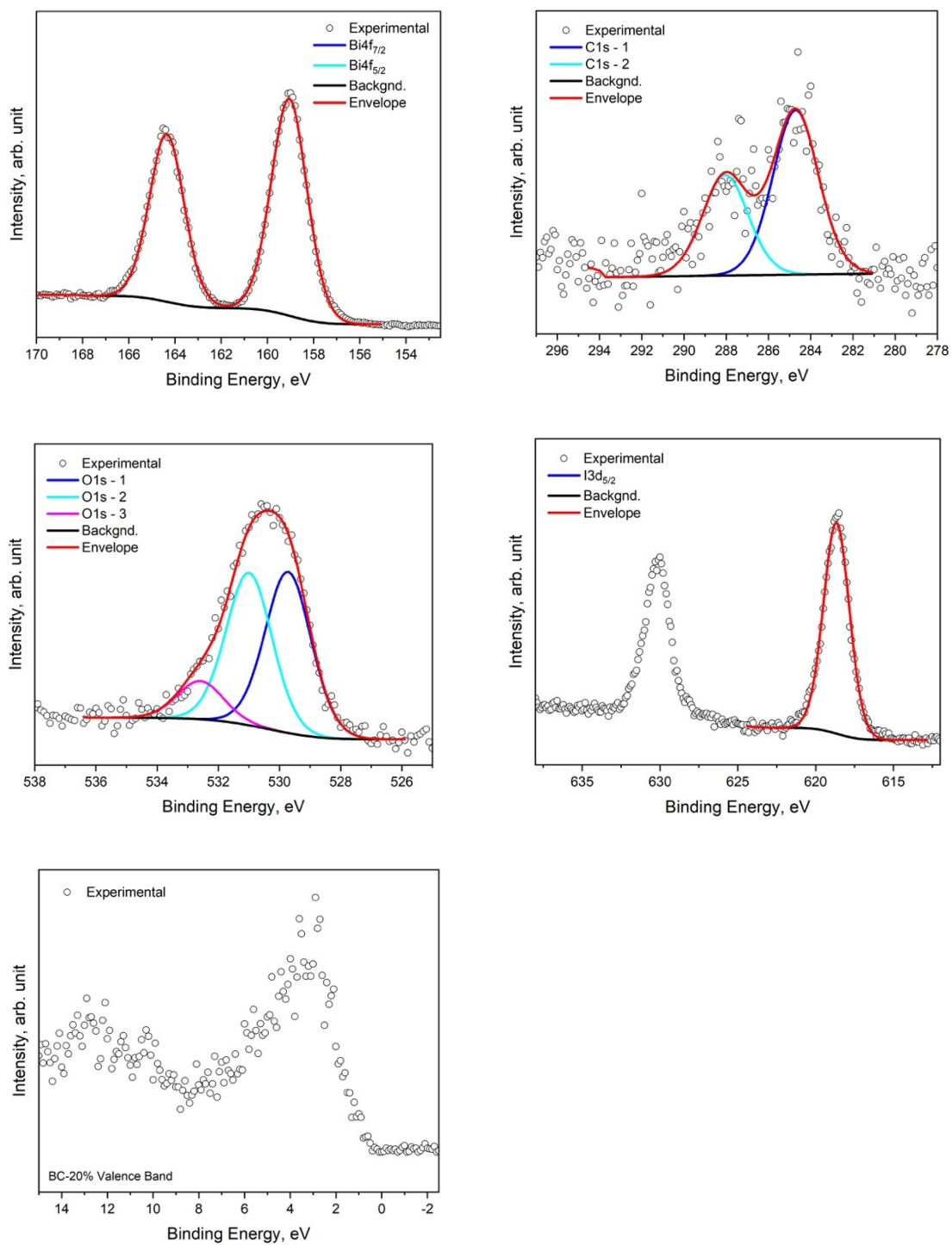


Figure S 6. XPS spectra of the composite BC-20%.

Peak	Peak BE (eV)	FWHM eV	Atomic %	State
Bi4f7	159.4	1.83	22.1	Bi <sub>2</sub> O <sub>3</sub>
C1s - 1	285.0	2.55	22.1	Aliphatic

C1s - 2	288.4	2.55	13.5	-C=O
I3d5	619.0	1.96	9.8	iodide
O1s - 1	530.0	1.77	14.9	oxides
O1s - 2	531.3	1.77	14.1	OH-, C-O
O1s - 3	532.7	1.77	3.5	H <sub>2</sub> O

*Table S 6. XPA quantification for the composite BC-20%.*

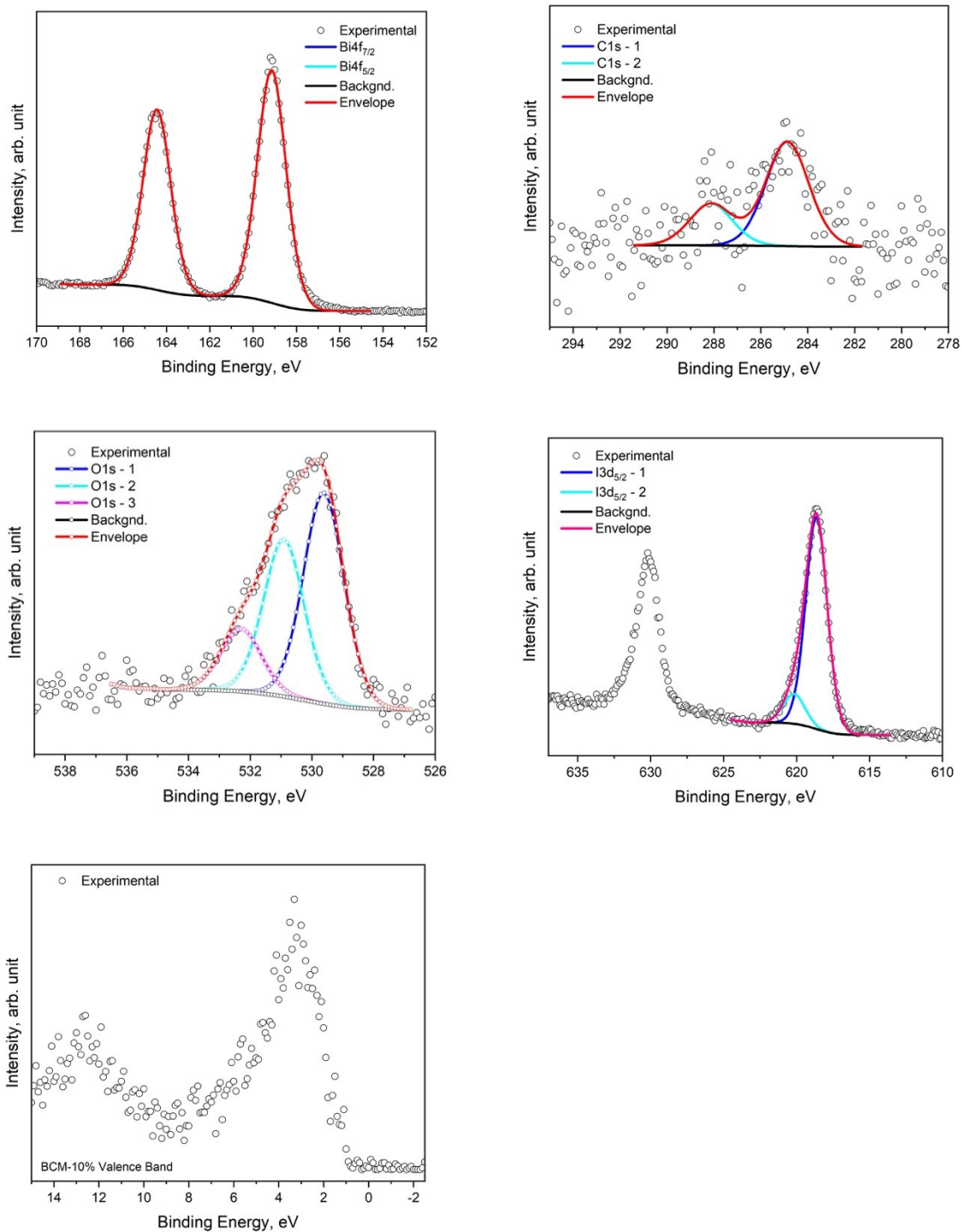


Figure S 7-XPS spectra of the composite BCM-10%.

Peak	Peak BE (eV)	FWHM eV	Atomic %	State
Bi4f7	159.2	1.56	28.6	Bi <sub>2</sub> O <sub>3</sub>
C1s - 1	285.0	2.16	14.5	Aliphatic

C1s - 2	288.2	2.16	5.8	-C=O
I3d5 - 1	618.7	1.73	15.3	iodide
I3d5 - 2	620.2	1.73	2.1	
O1s - 1	529.7	1.55	16.5	oxides
O1s - 2	531.0	1.55	12.3	OH <sup>-</sup> , C-O
O1s - 3	532.4	1.55	4.9	H <sub>2</sub> O

*Table S 7. XPS quantification of of the composite BCM-10%.*

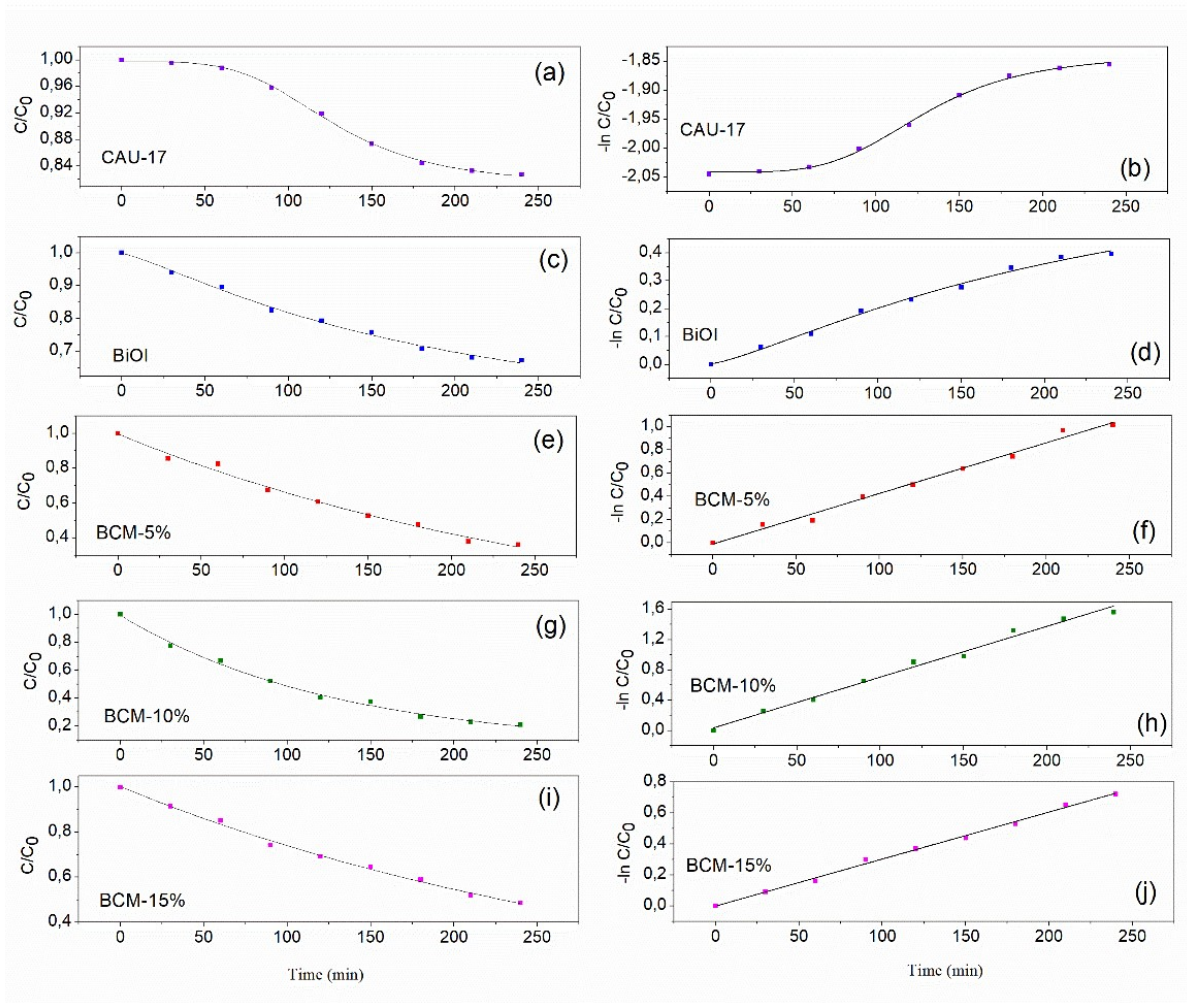


Figure S 8. Reaction course for the degradation of CIP upon light irradiation for pure CAU-17 (a-b), BiOI (b-c) and the ternary composites (e-g). Markers are experimental points, lines are fitting curves.

Table S 8. Fitting parameters of plots,  $C_t/C_0$  and  $\ln C_t/C_0$  vs Time, for CIP degradation for pure BiOI, CAU-17, and the ternary composites.

Sample	$C_t/C_0$ vs Time		$\ln C_t/C_0$ vs Time	
	Fitting Equations	Fitting parameters	Fitting Equations	Fitting parameters
CAU-17	sigmoidal	A1 = 0,9972 A2 = 0,8123 x0 = 126,5179 p = 4,0683 R <sup>2</sup> = 0,9977	sigmoidal	A1 = -2.0417 A2 = -1.83813 x0 = 129.3595 p = 4.13575 R <sup>2</sup> = 0.99778
BiOI	sigmoidal	A1 = 0.99848 A2 = 0.41821 x0 = 188.35225 p = 1.25727 R <sup>2</sup> = 0.9927	sigmoidal	A1 = 0.0023 A2 = 0.79818 x0 = 233.33609 p = 1.2967 R <sup>2</sup> = 0.99175
BCM-5%	exponential	Y0 = -0.1770 A1 = 1.1727 t1 = 298.498 R <sup>2</sup> = 0.9871	Linear	a = -0.01122 b = 0.00436 R <sup>2</sup> = 0.98829
BCM-10%	exponential	Y0 = 0.0527 A1 = 0.9409 t1 = 129.0638 R <sup>2</sup> = 0.9935	Linear	a = 0.03388 b = 0.00671 R <sup>2</sup> = 0.98885
BCM-15%	exponential	Y0 = -0.00065 A1 = 1.0024 t1 = 329.7704 R <sup>2</sup> = 0.9949	Linear	a = -0.00179 b = 0.00304 R <sup>2</sup> = 0.9956
<p>Fitting equations:</p> <p>Linear: <math>y = a + bx</math></p> <p>Exponential: <math>y = y_0 + A_1 e^{-\frac{x}{t_1}}</math></p> $y = \frac{A_1 - A_2}{1 + \left(\frac{x}{x_0}\right)^p} + A_2$ <p>Sigmoidal:</p>				

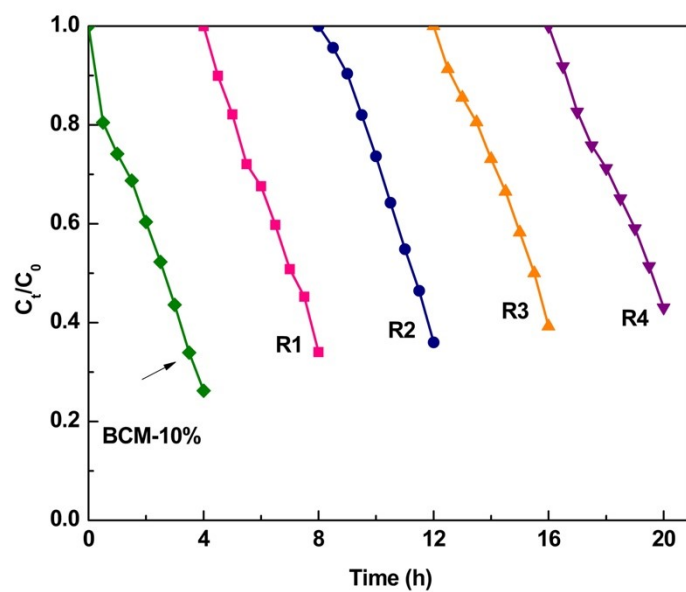


Figure S 9. Recycling efficiency of the photocatalyst BCM-10%.

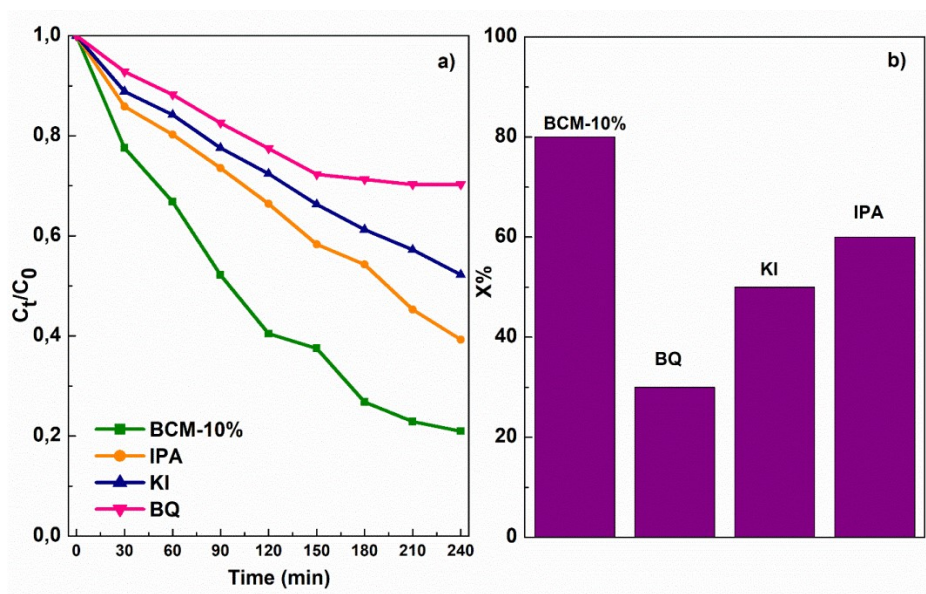


Figure S 10. Results of the catalytic tests carried out with the addition of scavengers. (a) Reaction course plotted as  $C_t/C_0$  vs. time and (b) degradation percentage as a function of the specific scavenger.

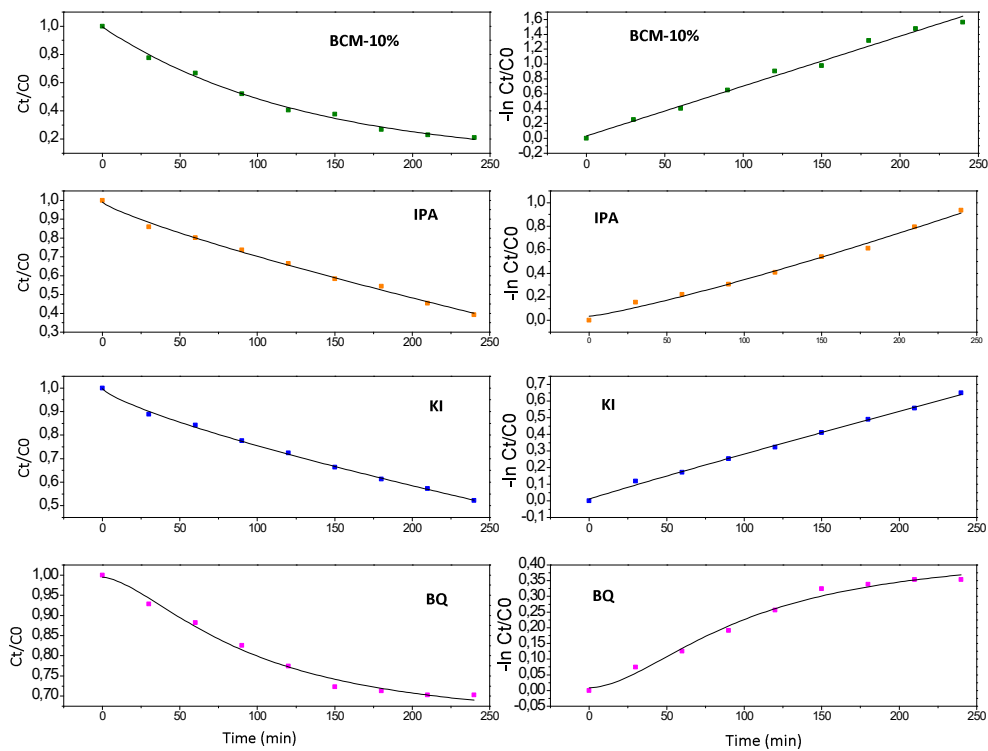


Figure S 11. Reaction course for the degradation of CIP upon light irradiation for BCM-10%, and with the addition of different IPA, KI and BQ scavengers. Markers are experimental points, lines are fitting curves.

Sample	$C_t/C_0$ vs. Time		$-\ln C_t/C_0$ vs. Time	
	Fitting Equations	Fitting parameters	Fitting Equations	Fitting parameters
BCM-10%	exponential	Y0 = 0.0527 A1 = 0.9409 t1 = 129.0638 R2 = 0.9935	Linear	a = 0.03388 b = 0.00671 R2 = 0.98885
BCM-10%, scavenger IPA	sigmoidal	A1 = 0.9906 A2 = -3911.81 x0 = 1.1212 p = 0.8183 R2 = 0.9929	sigmoidal	A1 = 0.0341 A2 = 25340,32 x0 = 1.4062 p = 1.1837 R2 = 0.9864
BCM-10%, scavenger KI	sigmoidal	A1 = 0.9970 A2 = -413.77 x0 = 1.6435 p = 0.7669 R2 = 0.9974	sigmoidal	A1 = 0.0101 A2 = 49580.97 x0 = 2.9581 p = 0.9616 R2 = 0.9960
BCM-10%, scavenger BQ	sigmoidal	A1 = 0.9949 A2 = 0.6198 x0 = 94.5863 p = 1.5835 R2 = 0.9833	sigmoidal	A1 = 0.0086 A2 = 0.4469 x0 = 100.9006 p = 1.7575 R2 = 0.9819

Table S 9. Fitting parameters of plots,  $C_t/C_0$  and  $\ln C_t/C_0$  vs Time for CIP degradation with the addition of scavengers For BCM-10% ternary composites

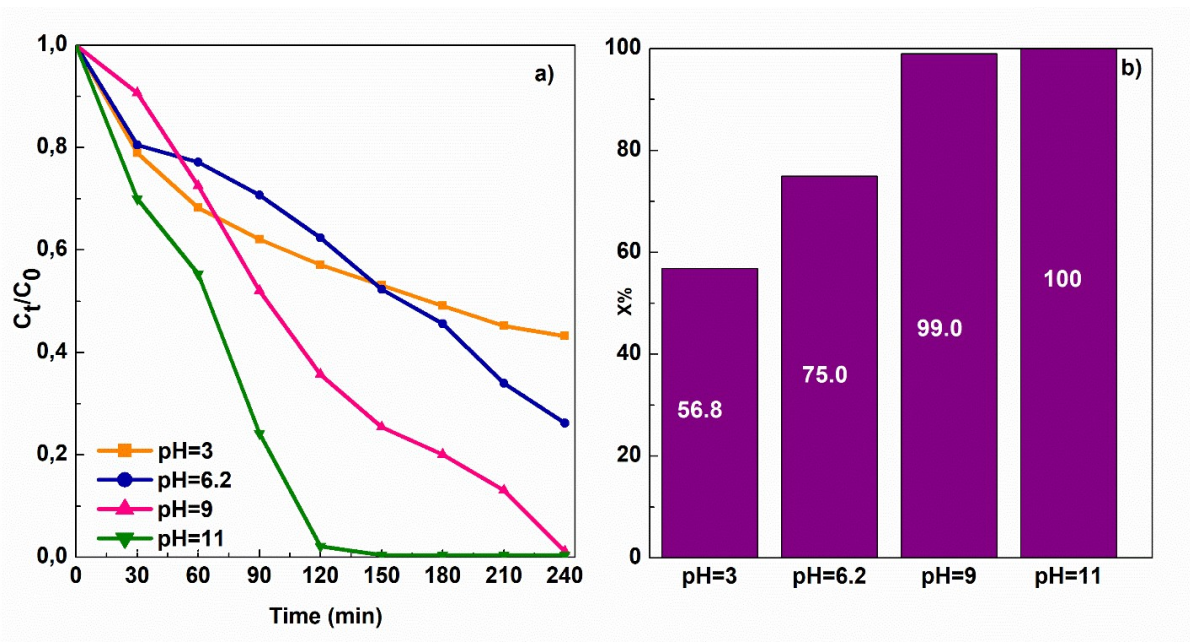


Figure S 12. Effect of pH on CIP photodegradation promoted by BCM-10%:(a) reaction course plotted as  $C_t/C_0$  vs. time and (b) removal efficiency at different pHs after 240 min reaction.

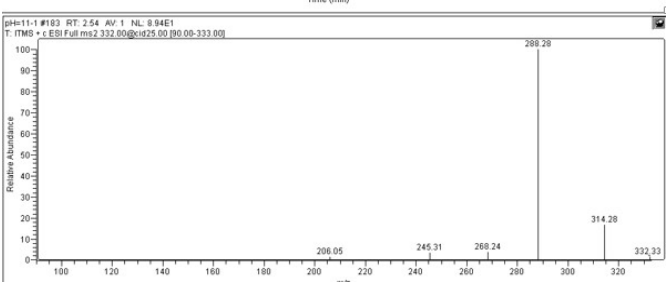
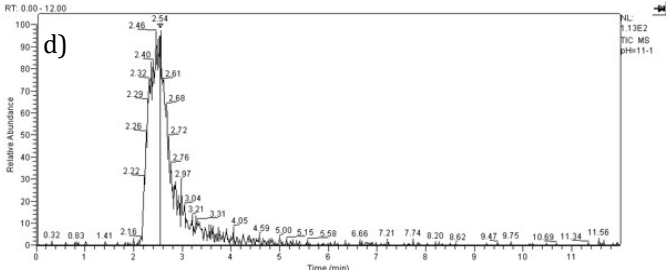
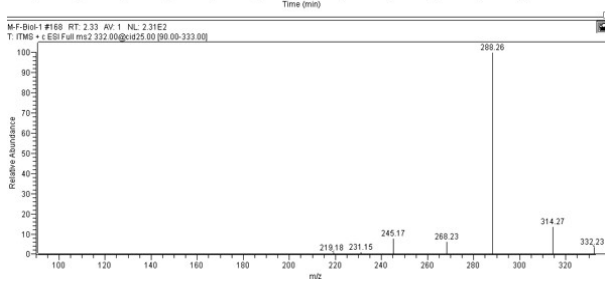
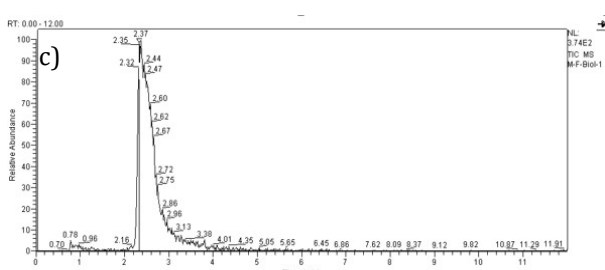
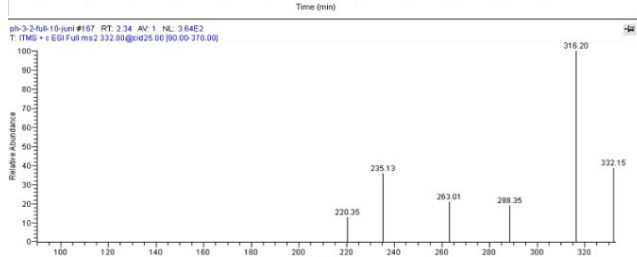
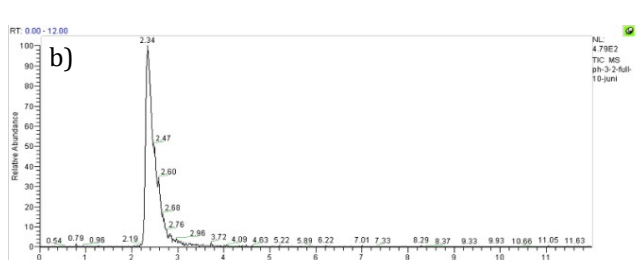
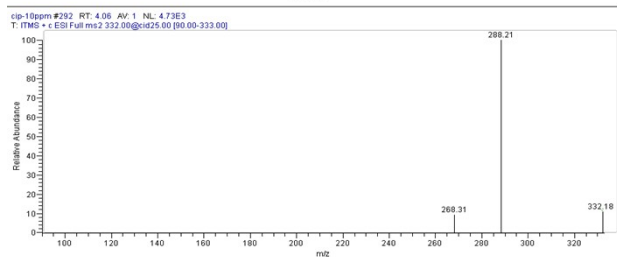
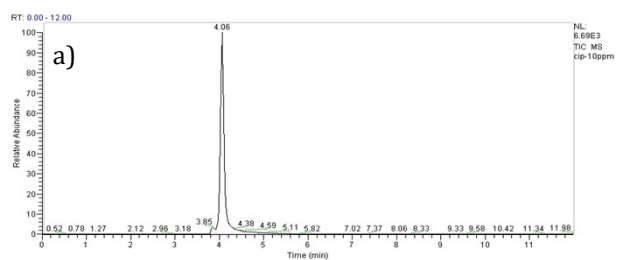


Figure S 13. Chromatograms and MS patterns pertaining to a) CIP and catalytic CIP degradation promoted by the ternary composite BCM-10% under simulated solar light at different pHs: b) pH= 3, c) pH = 6.2, d) pH=9,11.