

Supporting Information

Visible light degradation of tetracycline and bisphenol A by a hybrid photocatalyst composed of orange peel biochar, clay, and C/N-doped titania

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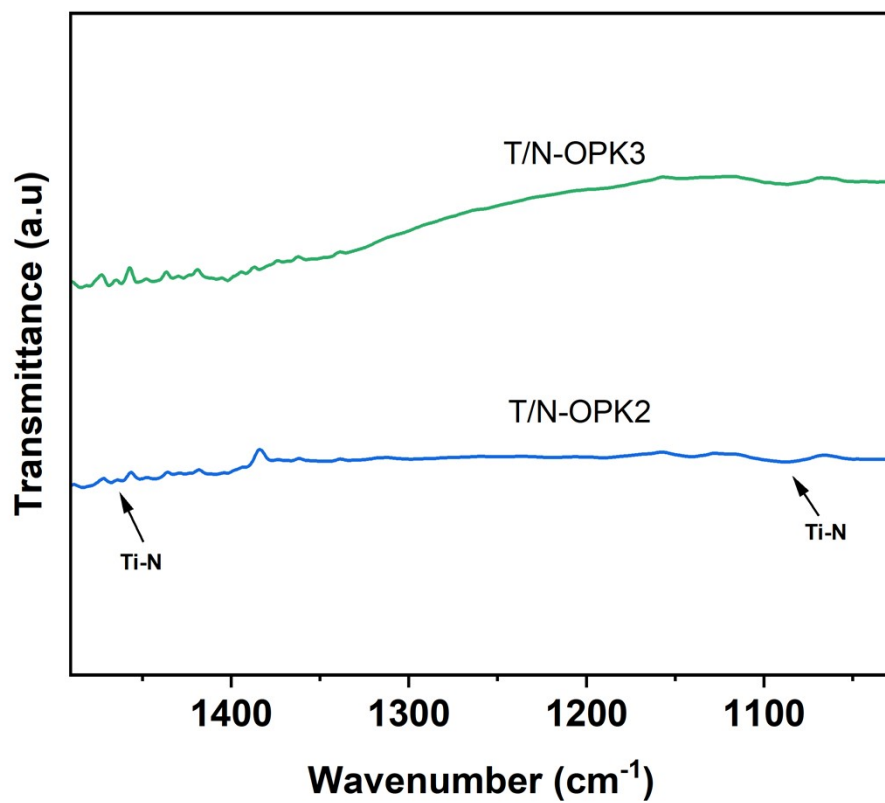


Figure S1: Enlarged FT-IR spectra of T/N-OPK2 and T/N-OPK3 in the range of 1490–1050 cm^{-1} .

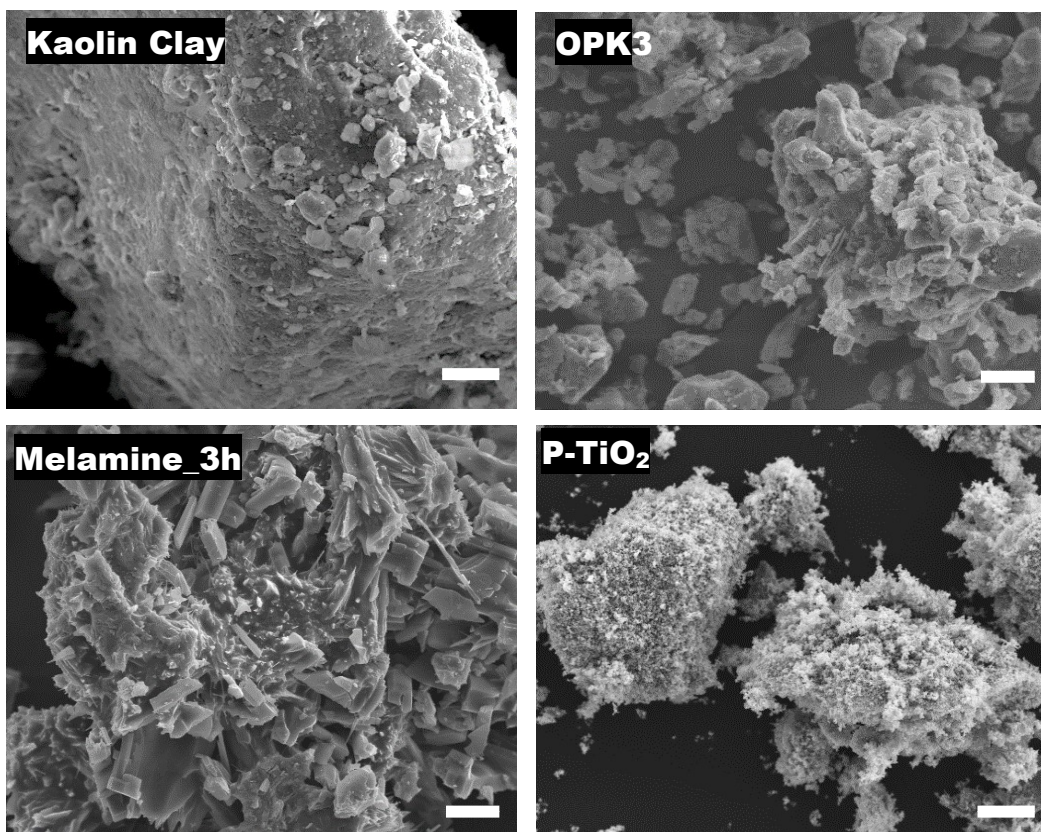


Figure S2: SEM images of pristine materials: kaolin clay, OPK3, Melamine_3h and P-TiO₂. The scale bar is 20 μm in all images.

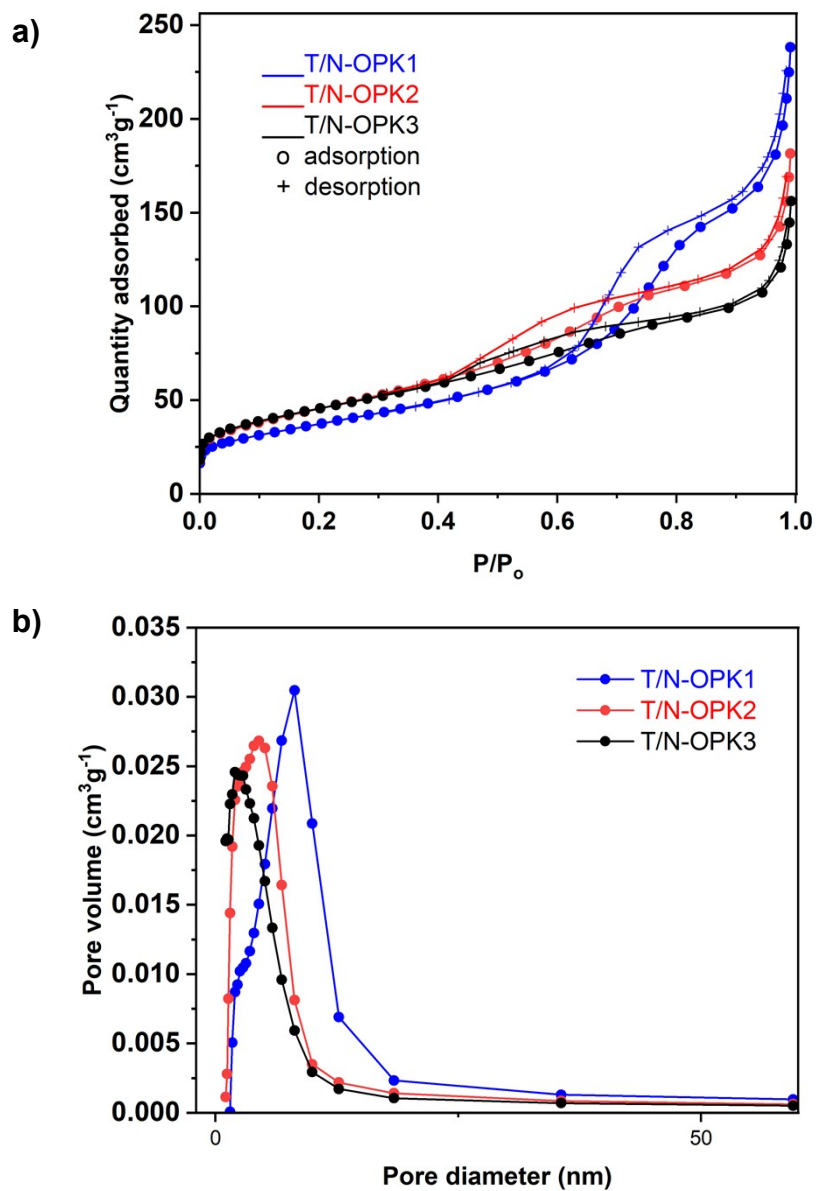


Figure S3: a) N_2 adsorption-desorption isotherms b) and corresponding BJH pore-size distributions of the photocatalyst composites.

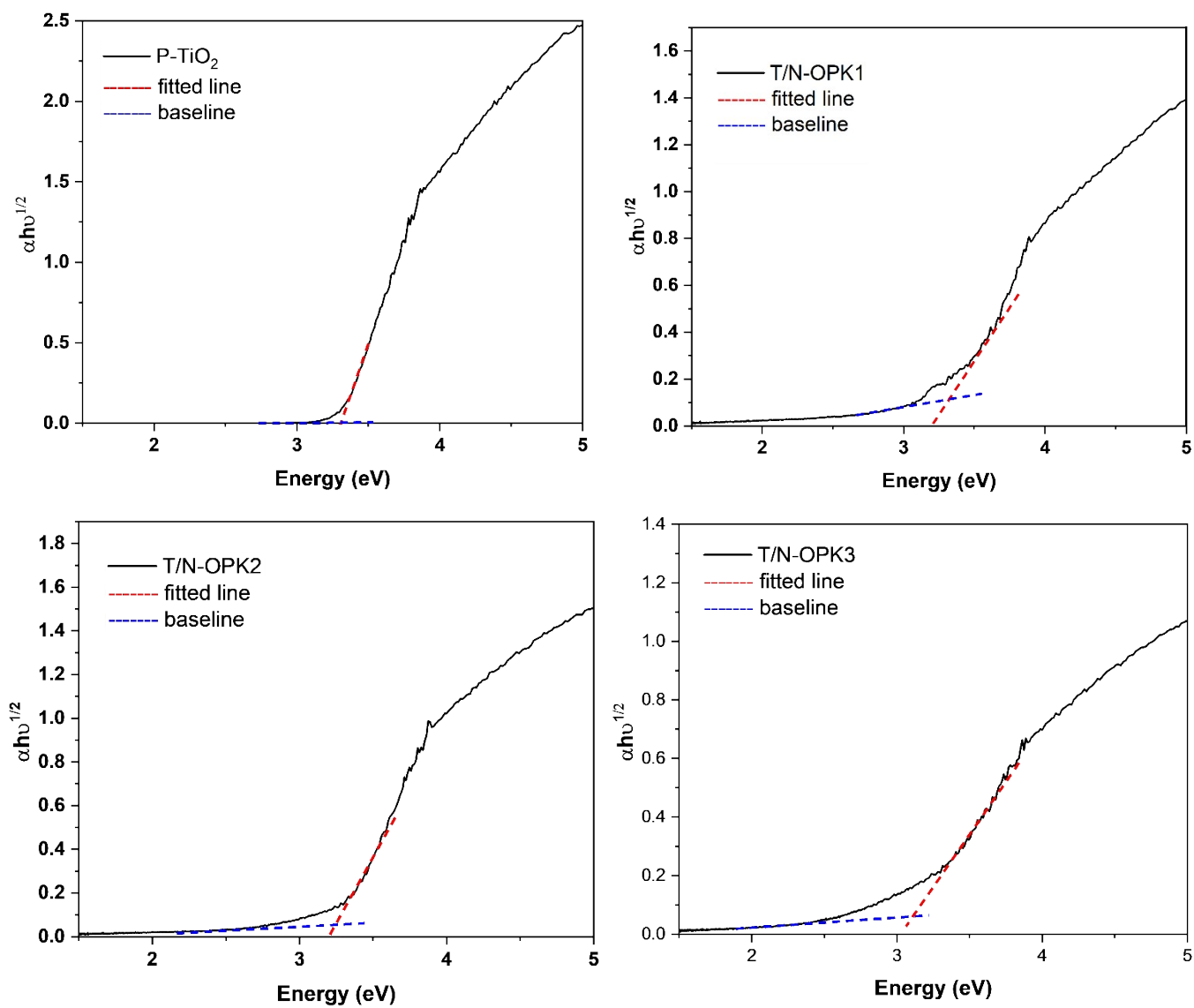


Figure S4: Tauc plots of the prepared photocatalyst. The determination of the E_g is shown.

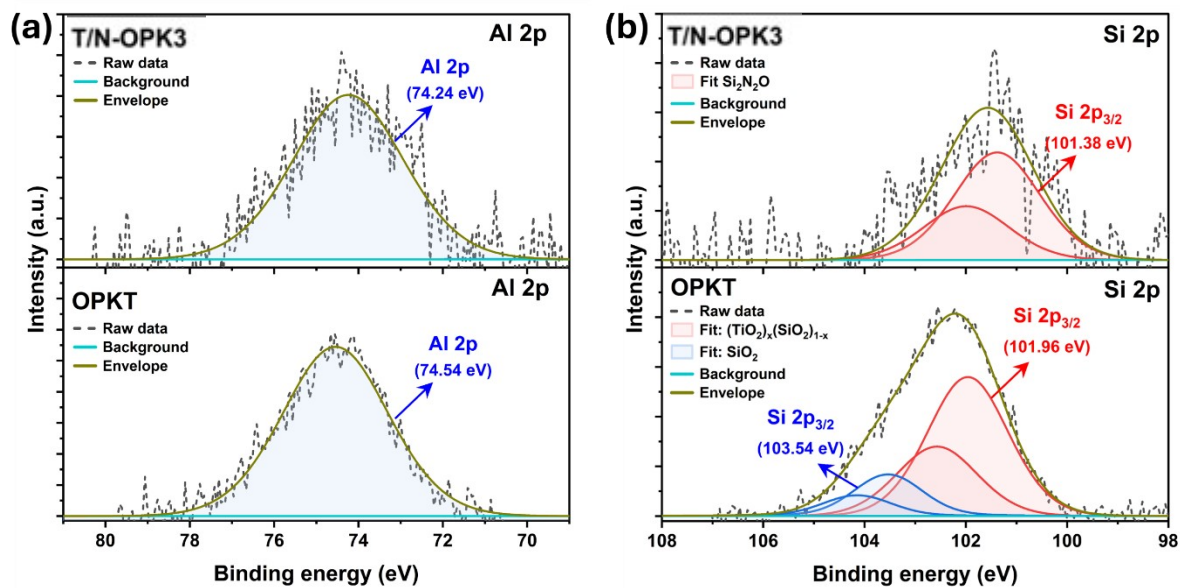


Figure S5: High-resolution XPS spectra of Al 2p (a) and Si 2p (b) in T/N-OPK3 and OPKT, respectively.

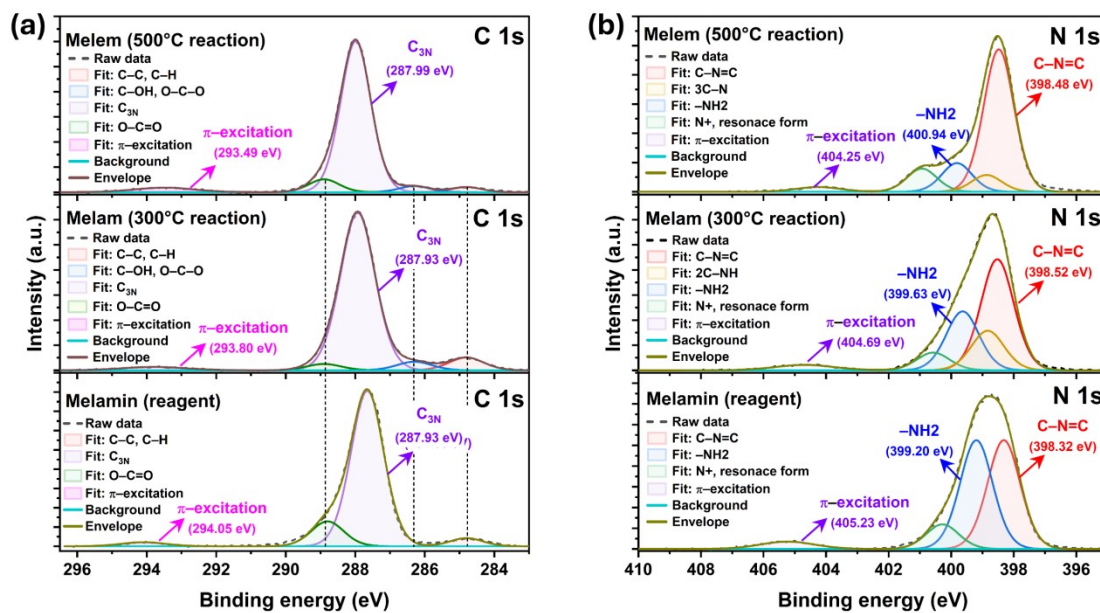


Figure S6: High-resolution XPS spectra of C 1s (a) and N 1s (b) in melamine, melam, and melem.

Scheme S1: Reaction scheme of melem and melam from melamine by thermal condensation, reproduced from previous literature.¹

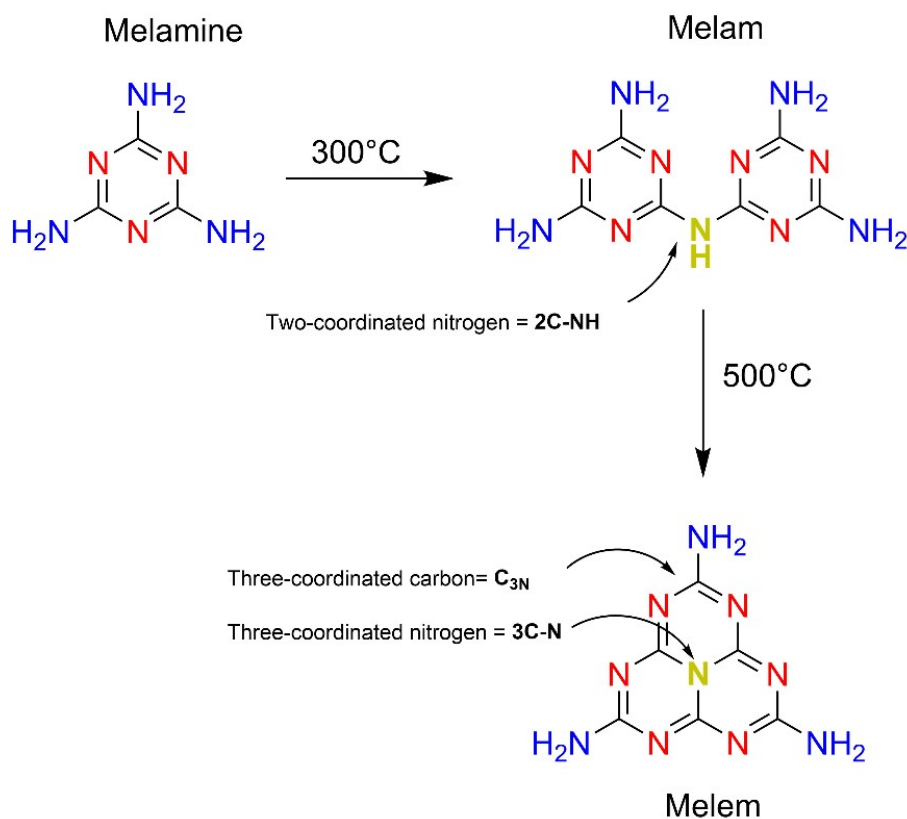


Table S1. Quantitative results of XPS measurements

Sample	Elemental composition (atomic %)*						Ratio (%) in Ti 2p	
	C	O	N	Ti	Si	Al	TiO ₂ (Ti ⁴⁺)	TiO _x N _{1-x} (Ti ³⁺)
OPKT	11.09	61.58	0.4	23.75	1.82	1.36	100.0	-
T/N-OPK3	18.78	50.37	8.97	19.49	0.07	2.33	70.13	29.87

* = Shirley background were applied for all the survey spectra

Table S2. XPS fitting parameters of the C 1s high-resolution spectra

Sample	Peak Assignment	Peak Identifier	BE (eV)	Peak Constraint (eV)	FWHM (eV)	FWHM Constraint (eV)	Area (%)	Atomic %	Line shape*
OPKT	Al-C-O	A	283.56	-	1.6	B*1	8.01	0.89	GL(30)
	C-C, C-H	B	284.8	284.8	1.6	0.9-1.6	57.25	6.35	GL(30)
	C-OH	C	286.3	B+1.5	1.6	B*1	16.55	1.84	GL(30)
	O-C=O	D	287.8	B+3	1.6	B*1	2.85	0.32	GL(30)
	C=O	E	288.8	B+4	1.6	B*1	13.26	1.47	GL(30)
	K impurity	F	292.98	-	1.48	0.9-1.6	2.07	0.23	GL(30)
T/N-OPK3	Al-C-O	A	283.56	-	1.6	B*1	15.43	2.90	GL(30)
	C-C, C-H	B	284.8	284.8	1.6	0.9-1.6	35.15	6.60	GL(30)
	C-OH	C	286.3	B+1.5	1.6	B*1	17.6	3.31	GL(30)
	C _{3N}	D	287.68	-	1.6	B*1	14.96	2.81	GL(30)
	O-C=O	E	287.8	B+3	1.6	B*1	2.15	0.40	GL(30)
	C=O	F	288.8	B+4	1.6	B*1	14.71	2.76	GL(30)

* = Shirley background were applied for all the C 1s high resolution spectra

Table S3. XPS fitting parameters of the N 1s high-resolution spectra

Sample	Peak Assignment	Peak Identifier	BE (eV)	Peak Constraint (eV)	FWHM (eV)	FWHM Constraint (eV)	Area (%)	Atomic %	Line shape*
Melamine	C-N=C	A	398.32	-	1.23	1.0-1.7	42.75	-	GL(30)
	-NH ₂	B	399.2	-	1.23	A*1	42.74	-	GL(30)
	N+, resonance	C	400.28	-	1.23	A*1	9.68	-	GL(30)
	pi excitation	D	405.23	-	2.06	0.7-2.2	4.84	-	GL(30)
T/N-OPK3	AlN	A	396.08	-	1.62	A*1	4.1	0.37	GL(30)
	TiOxN _{1-x}	B	397.27	-	1.62	A*1	16.84	1.51	GL(30)
	C-N=C	C	399.53	-	1.62	1.0-1.7	33.62	3.02	GL(30)
	-NH ₂ , N _i -H	D	400.73	-	1.62	A*1	33.75	3.03	GL(30)
	Ti-O-N, N+	E	398.36	-	1.62	A*1	11.7	1.05	GL(30)

* = Shirley background were applied for all the N 1s high resolution spectra

Table S4. XPS fitting parameters of the Ti 2p high-resolution spectra

Sample	Peak Assignment	Peak Identifier	BE (eV)	Peak Constraint (eV)	FWHM (eV)	FWHM Constraint (eV)	Area (%)	Area Constraint	Atomic %	Line shape*
OPKT	TiO ₂ (2p _{3/2})	A	458.59	A	1.2	0.9-1.2	66.69	A	15.84	GL(30)
	TiO ₂ (2p _{1/2})	B	464.31	A+5.72	2.13	1.9-2.2	33.31	A*0.5	7.91	GL(30)
T/N-OPK3	TiO _x N _{1-x} (2p _{3/2})	A	457.35	A	1.2	C*1	19.92	A	3.88	GL(30)
	TiO _x N _{1-x} (2p _{1/2})	B	463.07	A+5.72	2.15	D*1	9.95	A*0.5	1.94	GL(30)
	TiO ₂ (2p _{3/2})	C	458.25	C	1.2	0.9-1.2	46.77	C	9.12	GL(30)
	TiO ₂ (2p _{1/2})	D	463.97	C+5.72	2.15	1.9-2.2	23.36	C*0.5	4.55	GL(30)

* = Shirley background were applied for all the Ti 2p high resolution spectra

Table S5: The kinetic parameter vs. catalyst for the degradation of BPA and TET

Contaminants	BPA				TET			
	Parameter/ Material	k (min ⁻¹)	Normalized k	$t_{1/2}$ (min)	R^2	k (min ⁻¹)	Normalized k min ⁻¹ g ⁻¹	$t_{1/2}$ (min)
T/N-OPK1	0.00596 ±	0.119 ± 5.62	116.275	0.985	0.481 ±	9.62 ±	1.441	0.99
	2.81 x 10 ⁻⁴	x 10 ⁻³			0.00154	0.0308		9
T/N-OPK2	0.0110 ±	0.20 ± 9.56	63.115	0.987	0.491 ±	9.82 ± 3.00	1.411	0.82
	4.78 x 10 ⁻⁴	x 10 ⁻³			0.150			8
T/N-OPK3	0.0128 ±	0.256 ±	54.310	0.985	0.274 ±	5.48 ±	2.567	1
	7.17 x 10 ⁻⁴	1.43 x 10 ⁻²			0.00031	0.00632		6
OPKT	0.000160±	0.00320 ±	4337.40	-	0.187 ±	3.74 ±	3.707	-
	7.51 x 10 ⁻⁴	1.50 x 10 ⁻²	4		0.0109	0.218		
P-TiO ₂	0.00025355	0.0051 ±	2733.11	-	0.0819	1.64 ±	8.461	-
	7 ± 2.04 x	4.08 x 10 ⁻³	3		±	0.282	538	

	10 ⁻⁴				0.0141			
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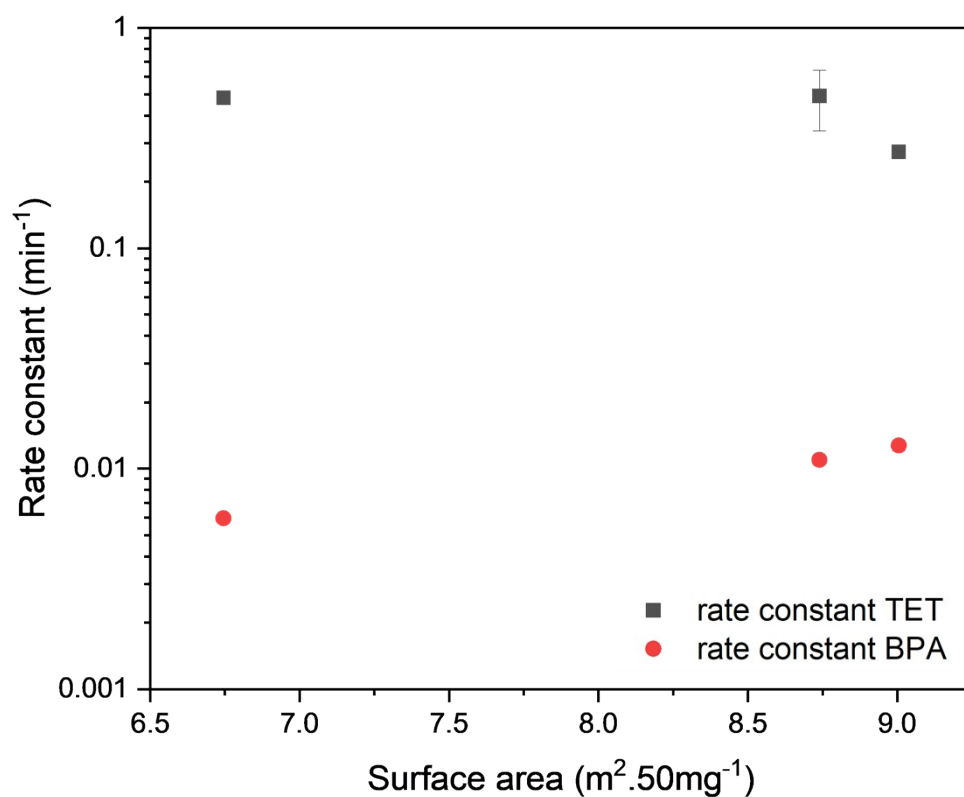


Figure S7: Direct correlation between surface area of the photocatalysts and rate constant, k .

Table S6: Equilibrium adsorption capacities (q_e) of BPA and TET on T/N-OPK catalysts under dark conditions

Catalyst	BPA (q_e , mg.g ⁻¹)	TET (q_e , mg.g ⁻¹)
T/N-OPK1	0.150	0.834
T/N-OPK2	0.122	0.801
T/N-OPK3	0.074	0.735

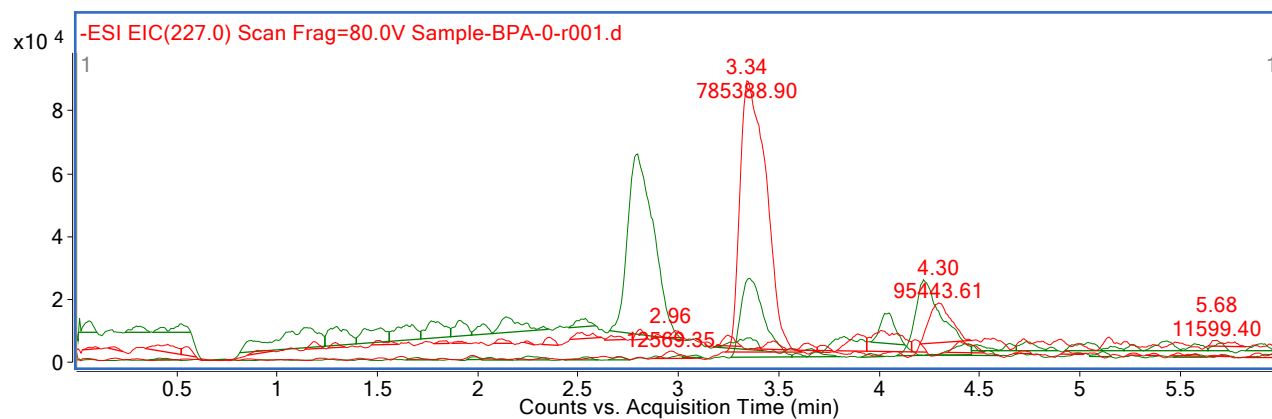


Figure S8: The extracted ion chromatogram of the LC-MS of the BPA solution before (red) and after (green) degradation using T/N-OPK3. The major mass is m/z 257 (breakdown products), as indicated in the following mass spectra in Figure S4 at the corresponding retention time.

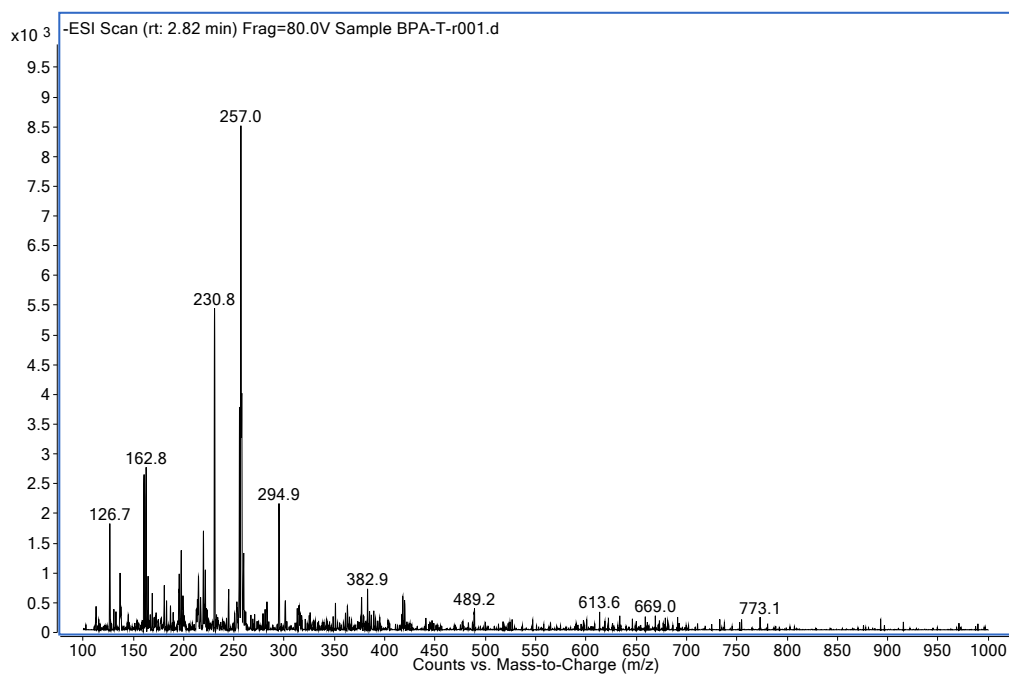


Figure S9: The extracted ion chromatogram of LC-MS of the intermediate product after degradation of 10 mg/L BPA solution using T/N-OPK3 at retention time 2.82 min.

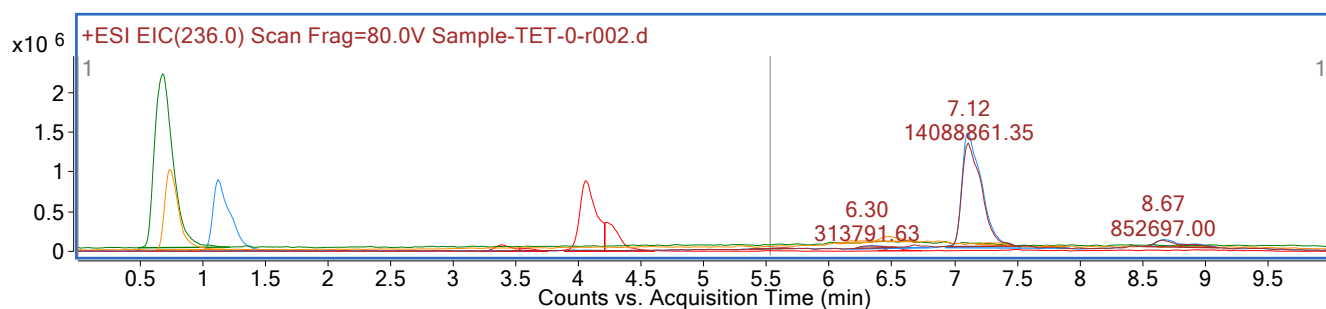


Figure S10: The extracted ion chromatogram of the LC-MS of the TET solution before (red) and after (other colors) degradation using T/N-OPK3. The major masses are m/z 127,169,236 (breakdown products) and 445.1 (control TET), as indicated in the following mass spectra in Figure S6-S7 at the corresponding retention times.

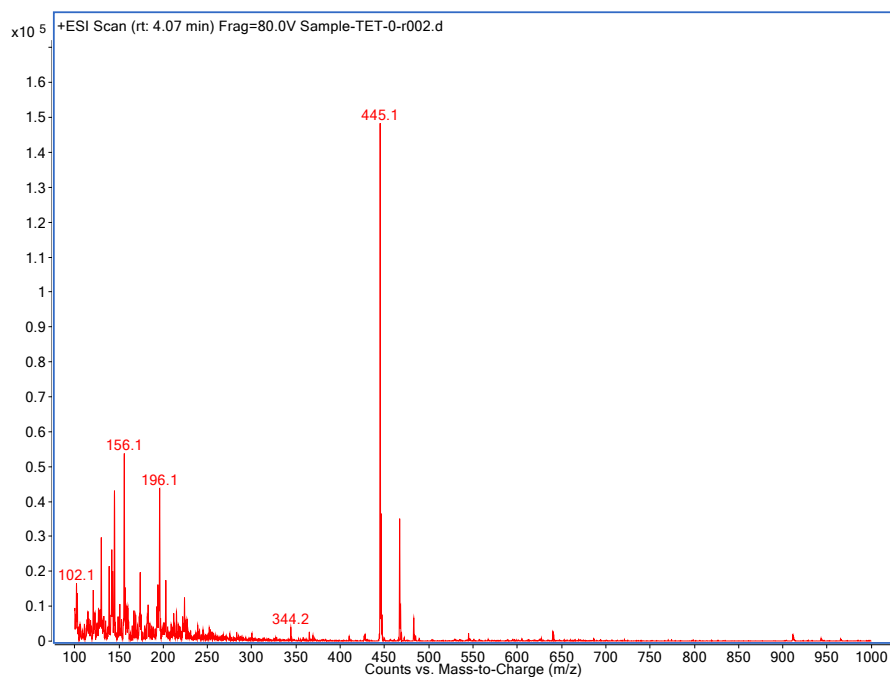


Figure S11: The extracted ion chromatogram of LC-MS of the control TET at retention time 4.07 min.

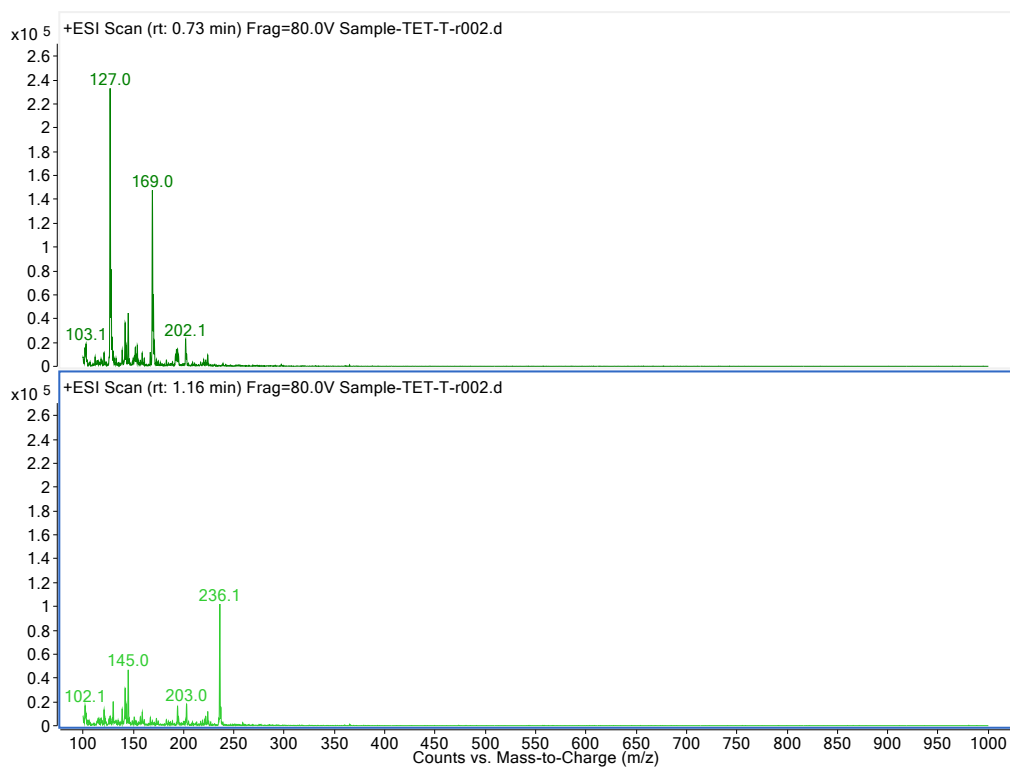


Figure S12: The extracted ion chromatogram of LC-MS of the intermediate product (a) and (b) at retention time 0.73 and 1.16 min, respectively.

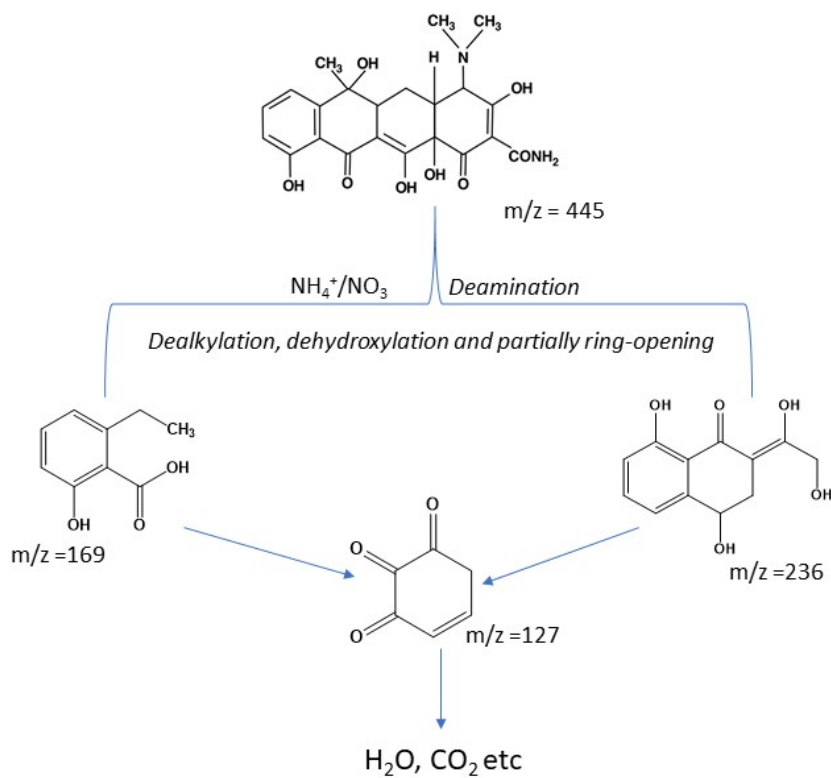


Figure S13: Proposed TET degradation pathway

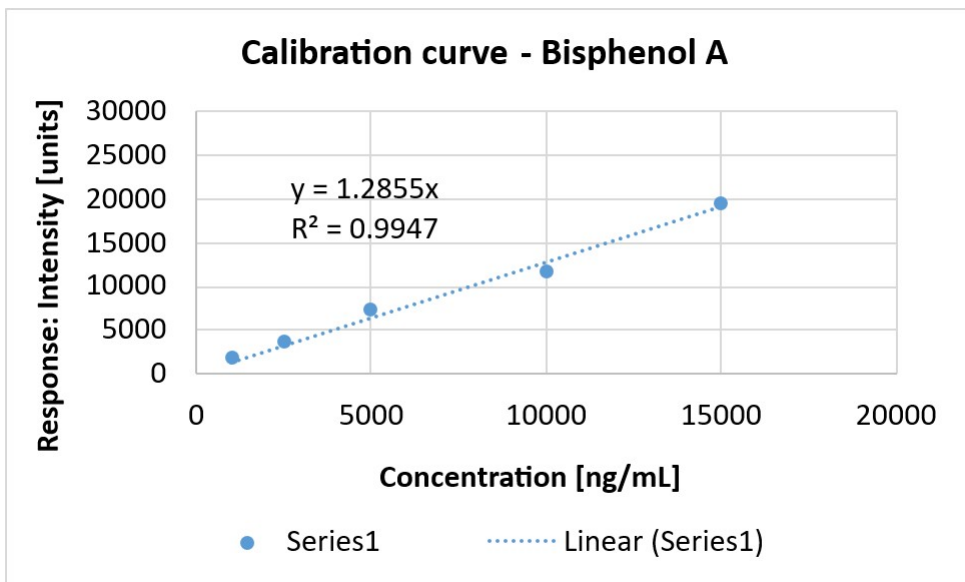
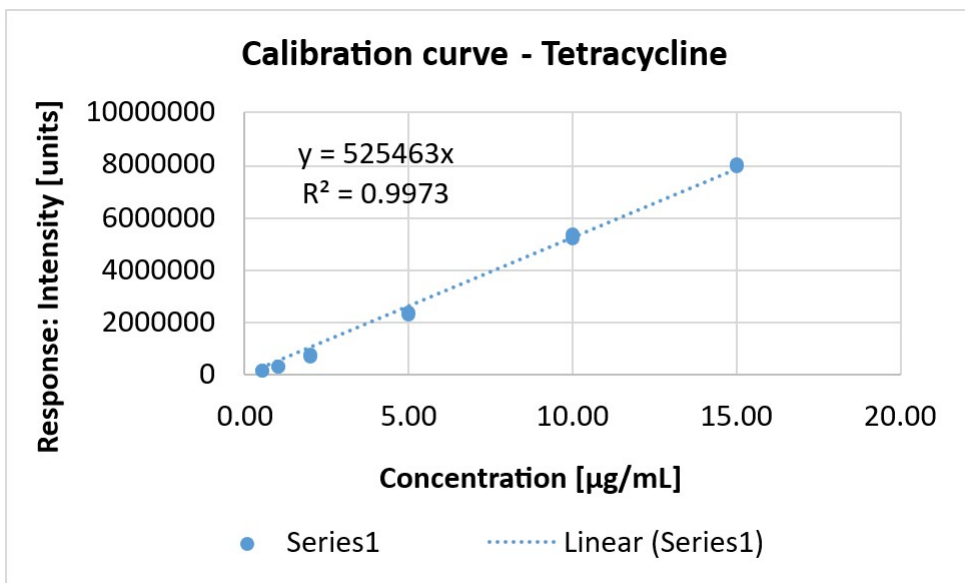


Figure S14: Calibration curve employed for Tetracycline (Calibration range is 0.5 $\mu\text{g/mL}$ - 15 $\mu\text{g/mL}$, LOD = 0.022 $\mu\text{g/mL}$) and Bisphenol A (Calibration range is 0.5 $\mu\text{g/mL}$ - 15 $\mu\text{g/mL}$, LOD = 0.043 $\mu\text{g/mL}$)

Table S7: The physicochemical properties of the various water matrices.

SAMPLES	pH	(TOC) (mg.L^{-1})	Temp ($^{\circ}\text{C}$)
Deionized water	7.0	8.116 ± 0.095	25
Tap water	7.2	20.914 ± 0.34	25
River water	7.0	20.225 ± 0.37	25

*Typical TOC value in drinking water may range from 0.1 to 25 mg.L^{-1} depending on regulatory compliance, matrix, quality and territory²

Table S8: Comparison of *T/N-OPK3* with Other TiO_2 Photocatalyst Composites

Photocatalyst	Contaminant	Reaction Condition	Surface area ($\text{m}^2.\text{g}$)	Degradation efficiency (%)	TOC removal (%)	Reference
N-doped MCMs@ TiO_2	Tetracycline	I.C = 80 $\text{mg}.\text{L}^{-1}$, I.T= 120 min, dosage= 50 mg	370	74.4	57	³
N-doped TiO_2 @C	Tetracycline hydrochloride	I.C = 15 $\text{mg}.\text{L}^{-1}$, I.T= 90 min, mass= 20 mg,	63	93	-	⁴
N-Doped Carbon Quantum Dots-Decorated TiO_2	Tetracycline	I.C = 10 $\text{mg}.\text{L}^{-1}$, dosage= 20 mg, , I.T= 120 min,	161.1	97.7	-	⁵
N-TiO_2/g-C_3N_4	Bisphenol A	I.C = 10 $\text{mg}.\text{L}^{-1}$, I.T= 240min, dosage = 0.5 $\text{g}.\text{L}^{-1}$	47.2	95.5	-	⁶
g-C_3N_4/TiO_2	Bisphenol A	I.C = 10 $\text{mg}.\text{L}^{-1}$, dosage=31.25 mg, I.T= 120 min	53	30.3	25.4	⁷
N-doped TiO_2-SiO_2	Bisphenol A	I.C = 10 $\text{mg}.\text{L}^{-1}$, dosage= I.T= 240 min	157	90.7	-	⁸
Cu-N/TiO_2	Bisphenol A	I.C = 10 $\text{mg}.\text{L}^{-1}$, dosage= 0.5 $\text{g}.\text{L}^{-1}$, I.T= 120 min	-	42.7	-	⁹
TiO_2/rice husk	Bisphenol A	I.C = 10 $\text{mg}.\text{L}^{-1}$, dosage= 0.5 $\text{g}.\text{L}^{-1}$, I.T= 60 min, ,	821	97.6	-	¹⁰
N-doped TiO_2/AC composite	Bisphenol A	I.C = 36 $\text{mg}.\text{L}^{-1}$ dosage= 0.25 $\text{g}.\text{L}^{-1}$ I.T= 180 min	559	59	-	¹¹
C600KT	Tetracycline	I.C = 20 $\text{mg}.\text{L}^{-1}$, dosage= 0.05g, I.T= 120 min	70.9	89	50	¹²
T/N-OPK3	Tetracycline	I.C = 10 $\text{mg}.\text{L}^{-1}$, dosage= 0.05g, I.T= 30 min	180	100	46	This study
T/N-OPK3	Bisphenol A	I.C = 10 $\text{mg}.\text{L}^{-1}$	180	82	50	This study

		, dosage= 0.05g, I.T= 120 min				
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References

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