

Electronic Supplementary Information

Catalytic Pulse Plasma Treatment for Organic Micropollutants: Unveiling the Synergistic Role of Photocatalysts in Radical Generation and Degradation Mechanisms

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2. Materials and Methods

2.7. Effect of wastewater system parameters

Total Alkalinity

The total alkalinity of the sample was analyzed using the titrimetric method. 20 mL of sample was titrated against 0.02 N H₂SO₄ using phenolphthalein and methyl orange indicators. The total alkalinity was calculated using Eq. S1 [1].

$$\text{Total alkalinity (mg/L as CaCO}_3\text{)} = \frac{\text{Volume of titrant (H}_2\text{SO}_4\text{)used} * 0.02 \text{ N} * 50000}{\text{Volume of sample}}$$

(S1)

Total Hardness

To measure the total hardness of wastewater, one or two drops of ammonia buffer was added to the 20 mL sample to increase the pH to around 10.0. The sample was titrated against 0.01 N EDTA using Eriochrome Black-T as indicator. At the end point, the solution turned from wine red to blue. The hardness was calculated using Eq. S2 [2].

$$\text{Total hardness (mg/L as CaCO}_3\text{)} = \frac{\text{Volume of titrant (EDTA) (mL)} * \text{Normality of EDTA} * 50000}{\text{Volume of sample (mL)}}$$

(S2)

Humic Acid

Humic acid was measured using UV Spectrophotometer (Shimadzu, Japan) by calibrating the known concentration against absorbance at 254 nm [3].

Cost Details

A. Catalyst

As per the latest sources local to our region following are the costs of the catalyst.

Cost of lab-grade TiO₂ = USD 480/kg

Cost of commercial TiO₂ (85:15 Anatase: Rutile) costs around USD3/ kg.

Cost of N-TiO₂(lab synthesis as per the methodology ¹⁴) USD 12080/kg

S. No.	Chemicals	Amount used during preparation	Expenses on the preparation (\$) #
a) Estimated preparation cost for N-TiO ₂ (for 0.5 g)			
1	Titanium Isopropoxide	2.4 mL	3
2	Ethanol	60 mL	1
3	Urea	0.8 g	0.12
4	HCl	2.5 mL	0.02
5	Energy costs (Vacuum Oven, Centrifuge)	19 kWh	1.9
Total =			6.04
Per g =			12.08

Cost based on prices from Sigma Aldrich website

B. Operational Cost

Batch Plasma Reactor

Step 1: Calculation of total amortized capital cost

Total amortized capital cost = capital cost + amortized cost

Cost analysis was carried out based on annual amortized cost, maintenance cost, and operating cost.

For the batch reactor, the total capital cost, including electrodes, casing, fittings, and engineering cost

(i) Electrodes cost = 62.5 \$

(ii) Casing, fittings, piping and engineering cost for 4 cm height x 5 cm Dia of 50 mL size reactor as per manufacturing pricing = 25 \$ (as per manufacturing pricing) (excluding electrode cost)

Therefore, the total capital cost = (i) + (ii) = 62.5 \$ + 25 \$ = 87.5 \$

$$\text{Amortized cost} = A = \frac{p * i * (1 + i)^{n-1}}{(1 + i)^n - 1}$$

The investment cost 'p' for batch reactor in original year is 87.5 \$ that including the cost of energy, material (electrodes, Plexiglas), chemicals casing, fitting, piping and engineering. The reactor life was considered for 10 years with an annual depreciation rate of 10%. (10 years because generally electrical-based items are considered for 10 years of life)

Therefore, the calculated amortized annual capital cost $A = 13$ \$

Step 2: Maintenance cost

In the present reactor, tungsten electrodes were used, which need annual replacements. The electrode replacement cost is considered to be 5000 INR

Therefore, maintenance cost = 62.5 \$ (as per manufacturing pricing)

Step 3: Annual operating cost

It was considered that the reactor operated for 8 hours daily with a treatment time of 15 min per batch.

Pulsed power plasma cost: Given input energy at 23 kV, 33 Hz frequency, and corresponding deposited energy is 0.01 kW for batch reactor

Therefore, the total annual electricity requirement is = 29.2 kWh, which corresponds to 2.92 \$

Therefore, annual operating cost = 2.9 \$/year

Step 4: Total treatment cost

Total annual treatment cost = annual amortized cost + maintenance cost + operating cost = 13 \$ + 62.5 \$ + 2.9 \$ = 78.4 \$/year

The total volume of wastewater treated = 584 L

Total water treatment cost/m³ = 134 \$/m³

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Figure S10. Mass spectra of reactive red 180 (RR180) solution and those treated by catalytic plasma discharge with N-TiO₂ after different treatment times (a) treated after 2 min (b) 4 min (c) 6 min (d) 8 min.

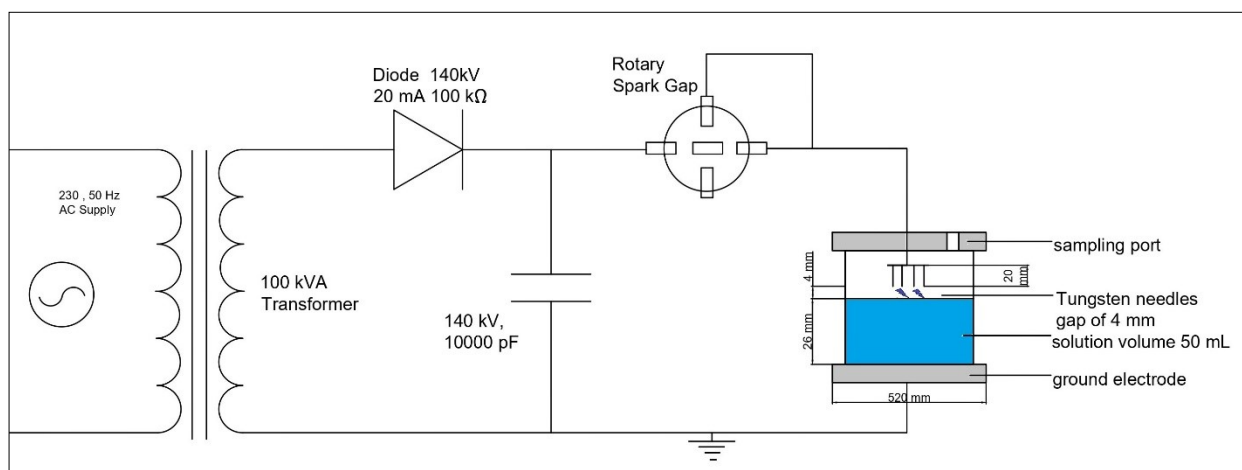


Fig. S1. Experimental setup and pulse plasma discharge circuit

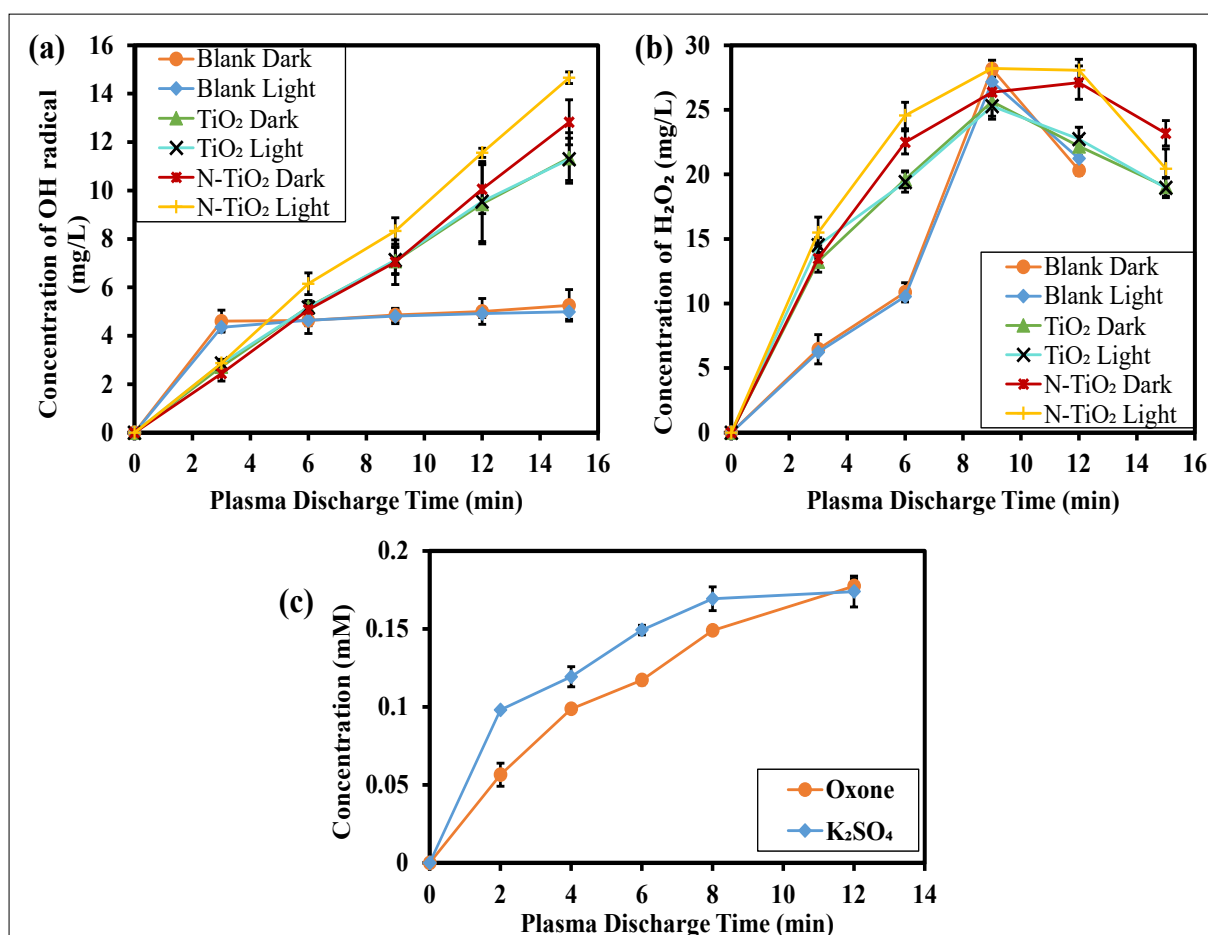


Fig. S2. Kinetics of accumulated (a) $\cdot\text{OH}$ (b) H_2O_2 (c) $\cdot\text{SO}_4^-$ (Applied voltage = 23 kV, frequency = 33 Hz)

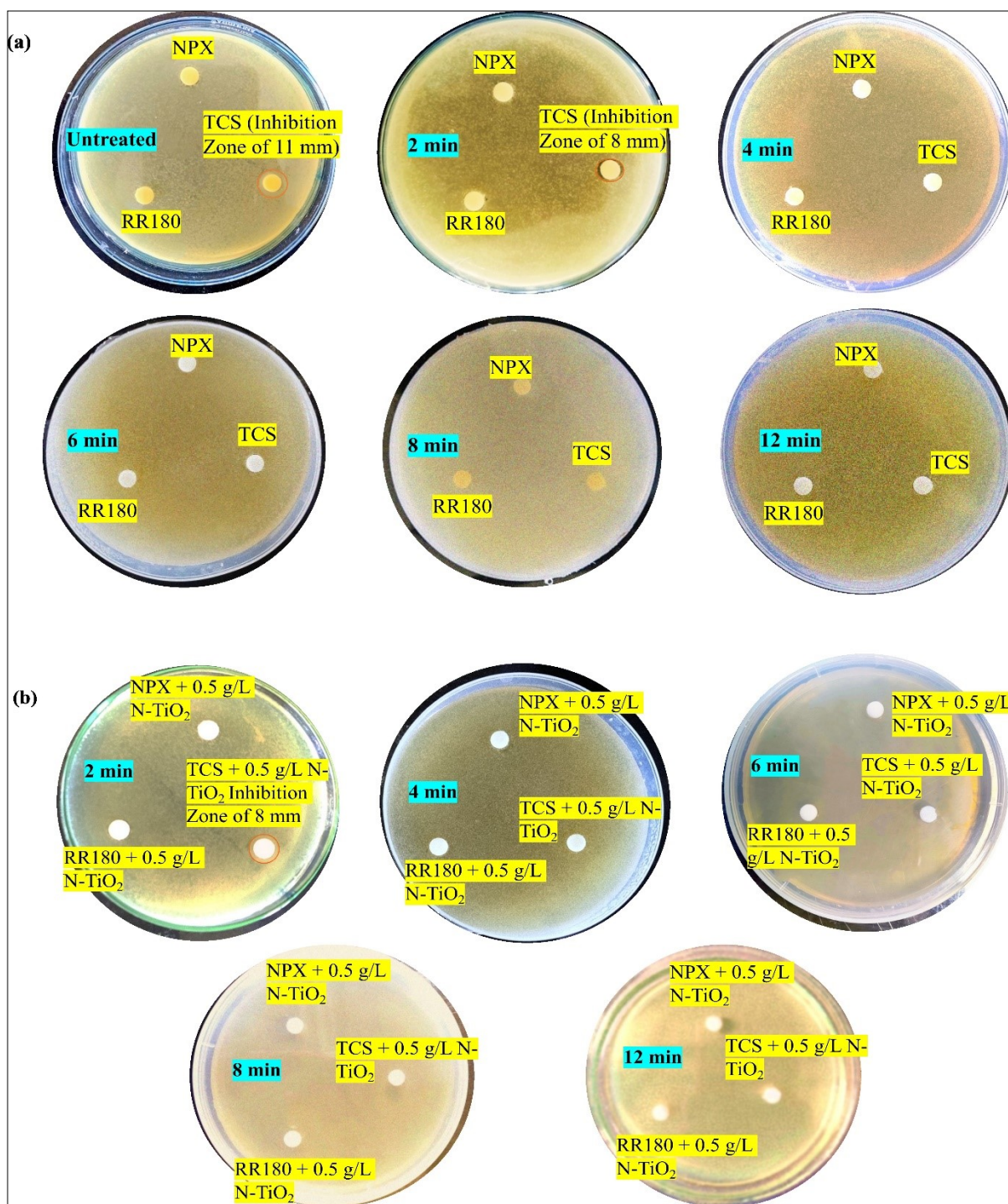


Fig. S3. Toxicity Assay for NPX, TCS, and RR180 (a) without catalyst (b) with N-TiO₂ for various time intervals

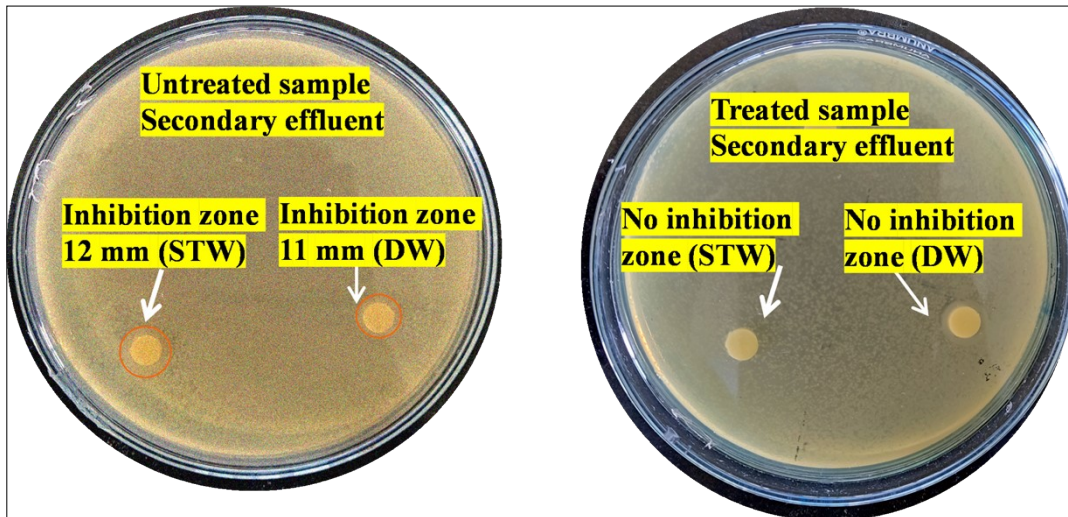


Fig. S4. Residual toxicity for secondary treated effluent (a) spiked untreated sample (b) plasma treated sample

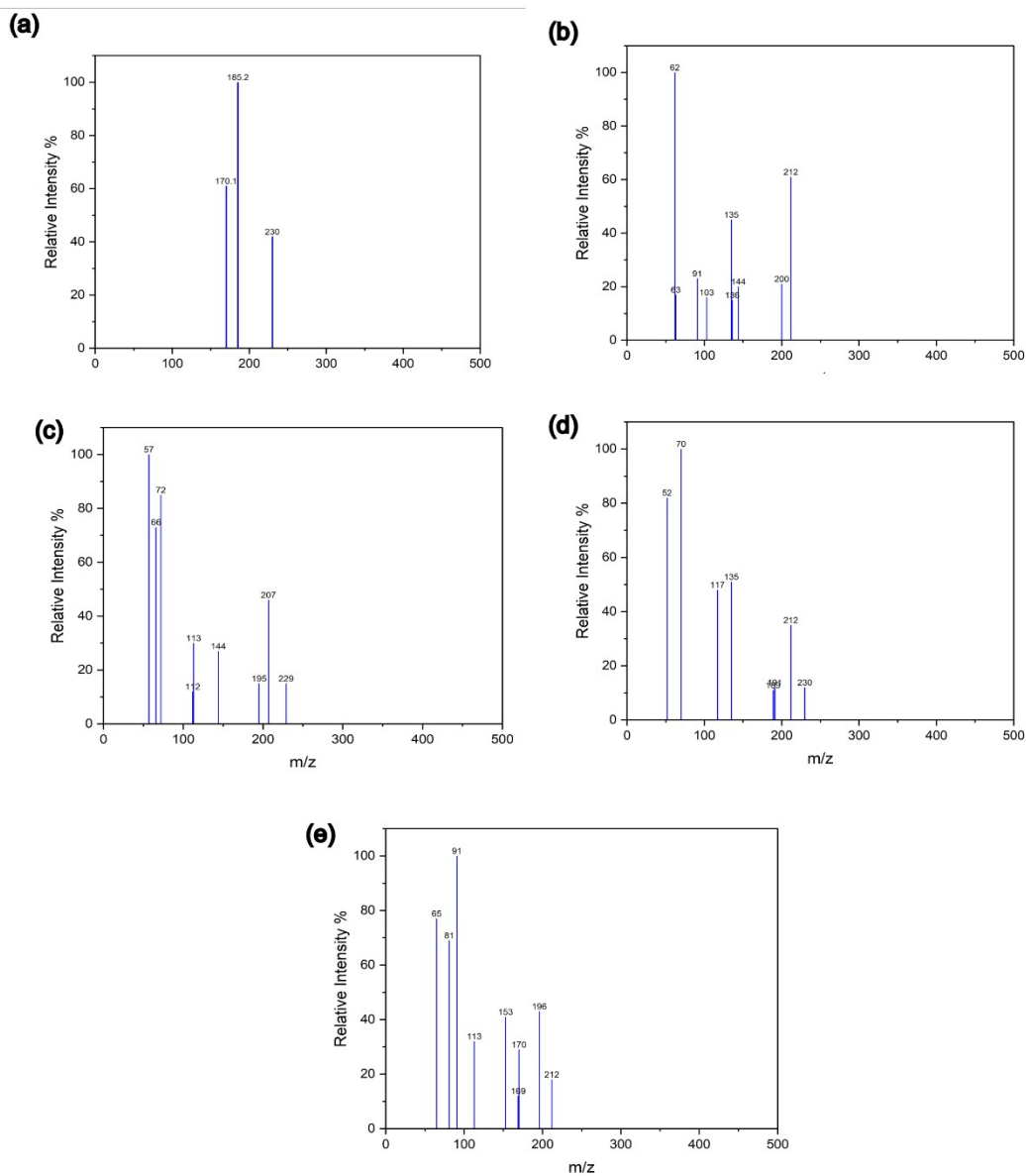


Fig.S5. Mass spectra of naproxen (NPX) solution and those treated by standalone plasma discharge after different treatment times (a) initial NPX solution (b) treated after 2 min (c) 4 min (d) 6 min (e) 8 min.

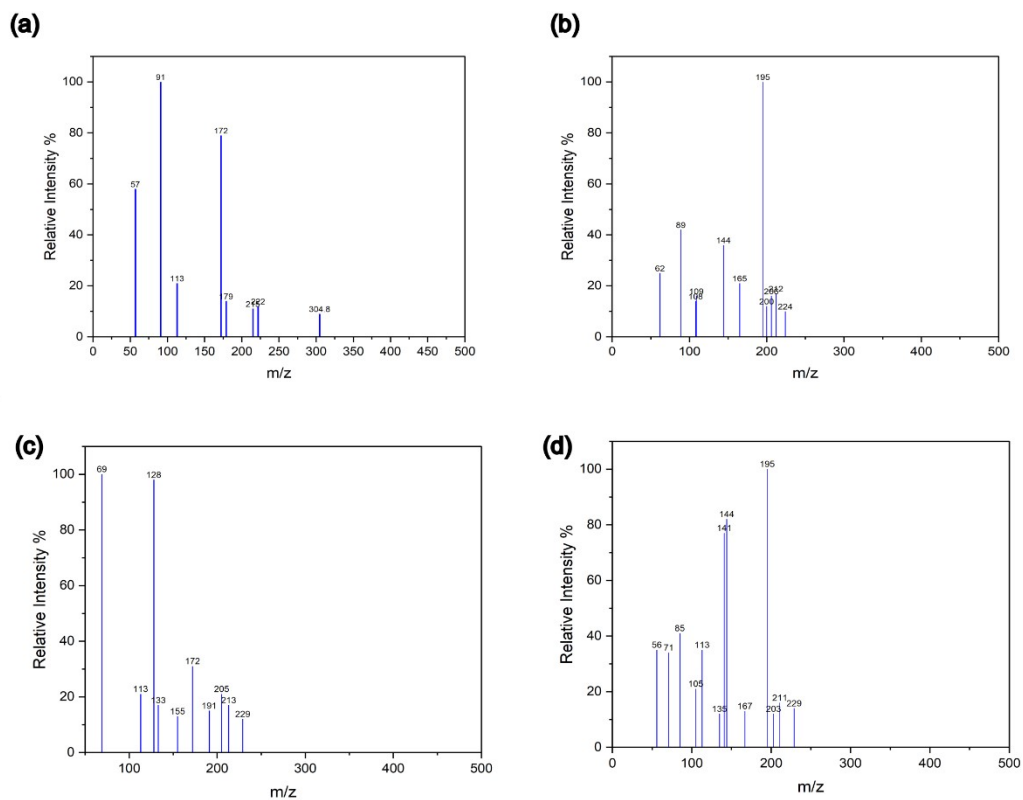


Fig. S6. Mass spectra of naproxen (NPX) solution and those treated by catalytic plasma discharge with N-TiO₂ after different treatment times (a) treated after 2 min (b) 4 min (c) 6 min (d) 8 min.

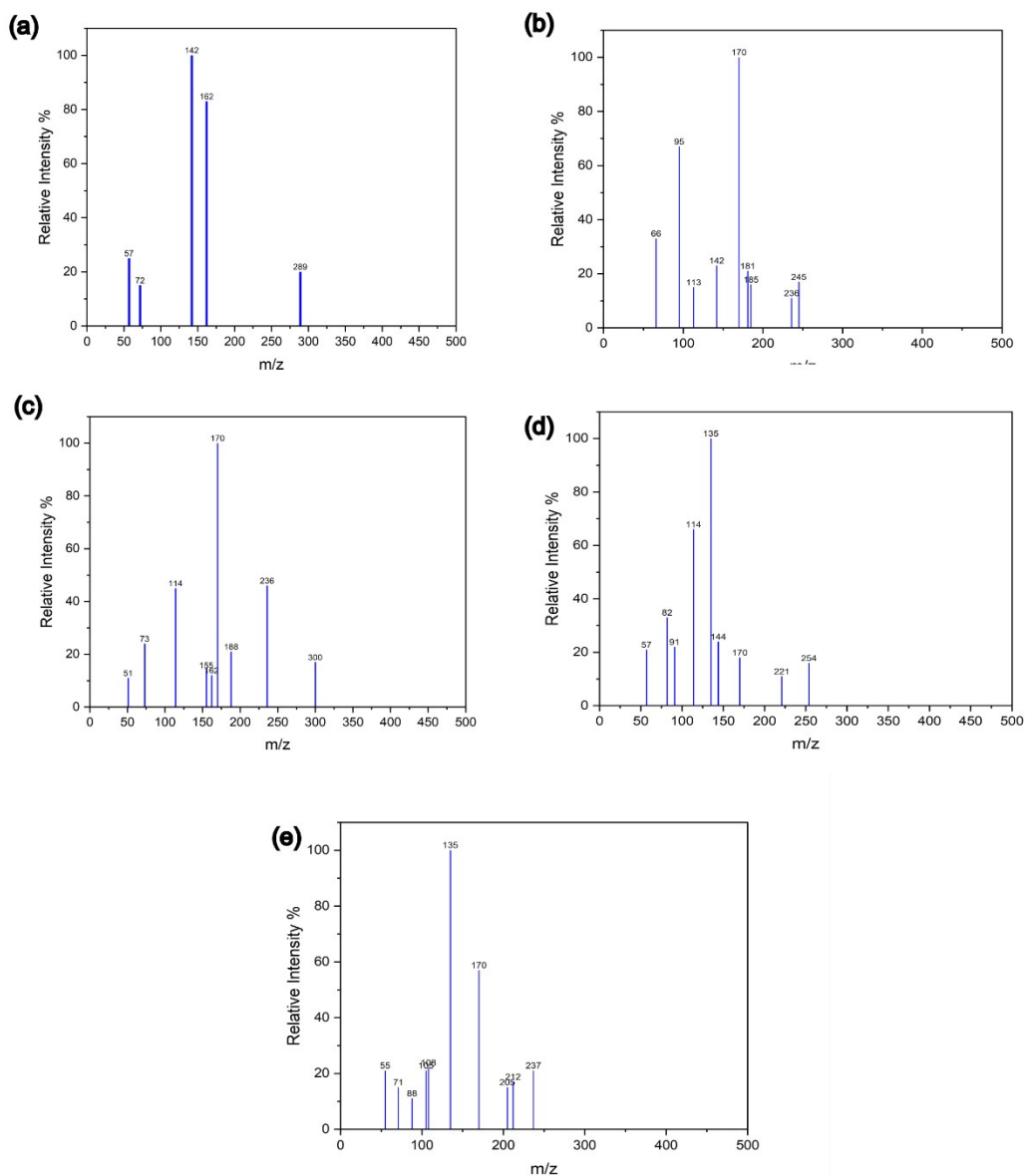


Fig. S7. Mass spectra of triclosan (TCS) solution and those treated by standalone plasma discharge after different treatment times (a) initial TCS solution (b) treated after 2 min (c) 4 min (d) 6 min (e) 8 min.

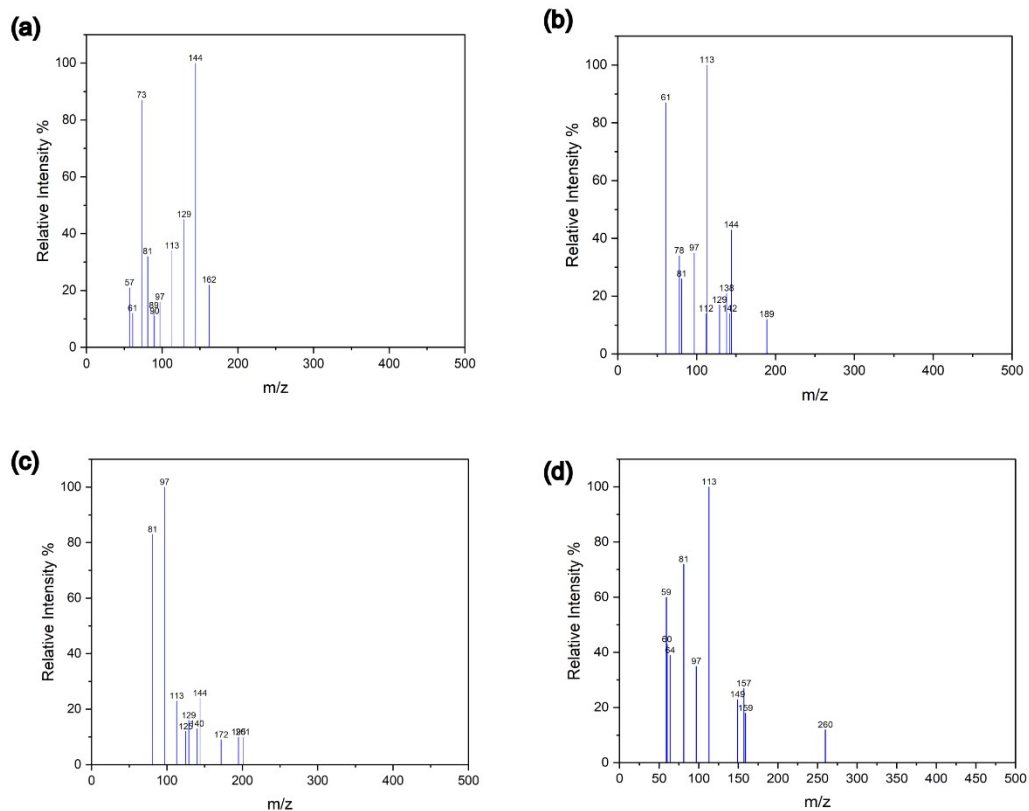


Fig. S8. Mass spectra of triclosan (TCS) solution and those treated by catalytic plasma discharge with N-TiO₂ after different treatment times (a) treated after 2 min (b) 4 min (c) 6 min (d) 8 min.

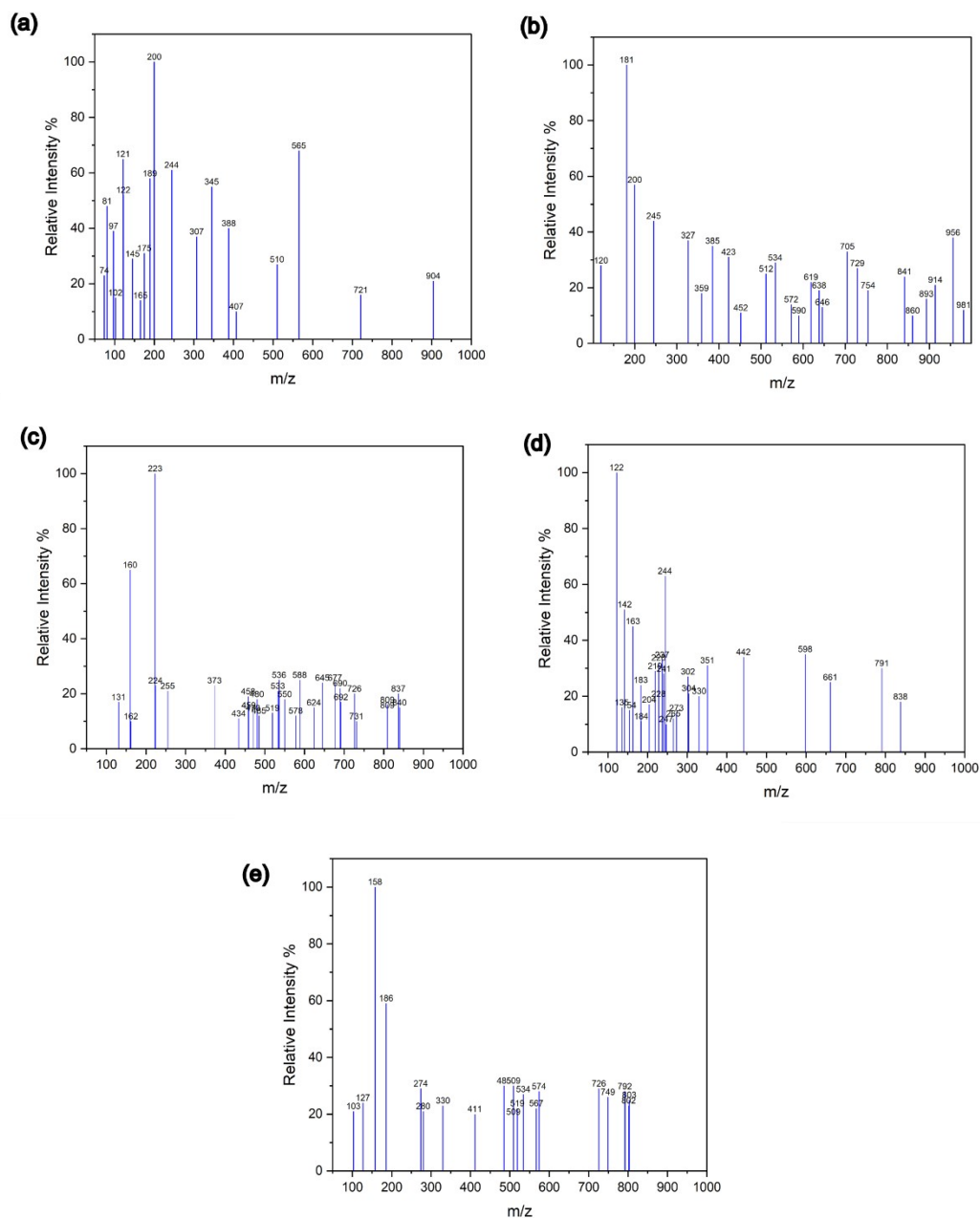


Fig. S9. Mass spectra of reactive red 180 (RR180) solution and those treated by standalone plasma discharge after different treatment times (a) treated after 2 min (b) 4 min (c) 6 min (d) 8 min (e) 12 min.

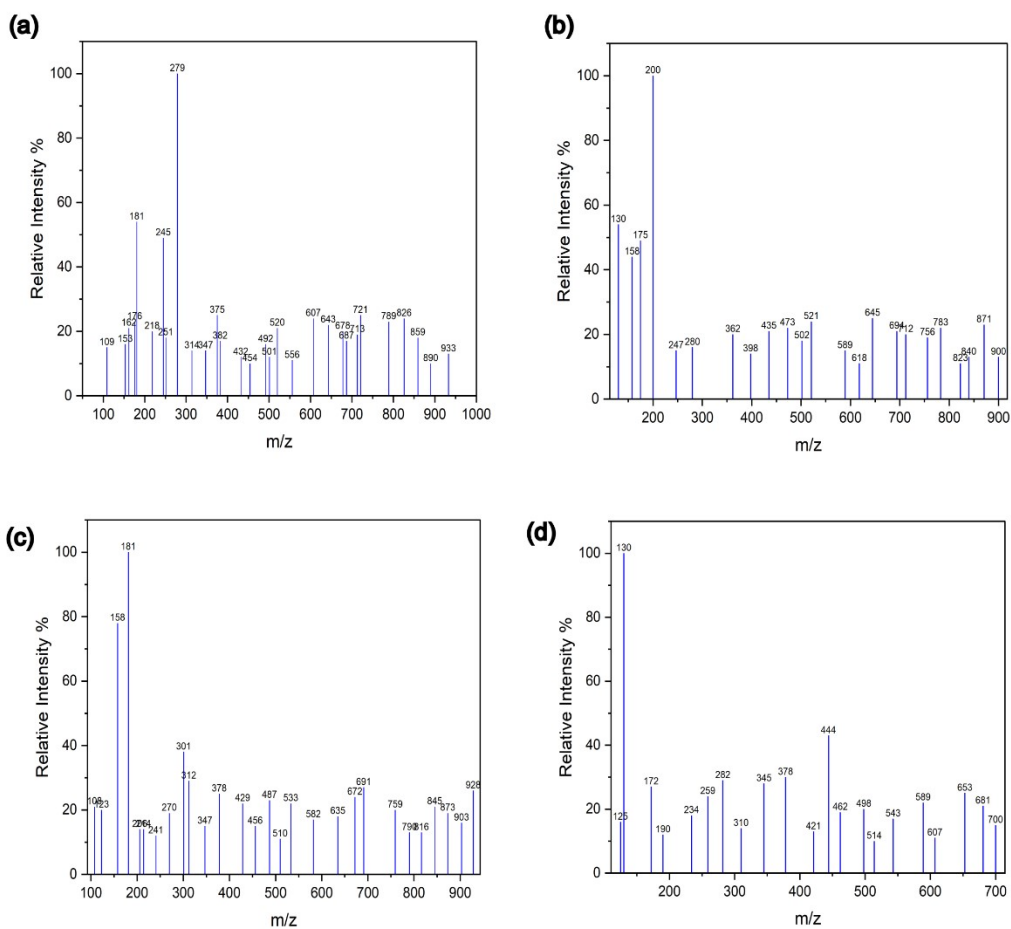


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Table S1. Physico-chemical properties of the pollutants in the study

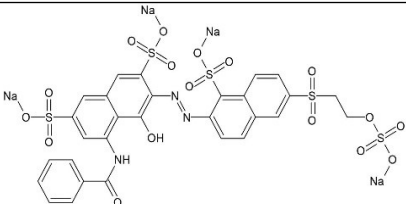
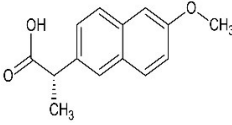
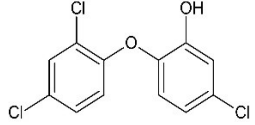
	Reactive Red 180 (RR180)	Naproxen (NPX)	Triclosan (TCS)
			
Mol. Formula	$C_{29}H_{19}N_3Na_4O_{17}S_5$	$C_{14}H_{14}O_3$	$C_{12}H_7Cl_3O_2$
Mol. Wt.	937.79	230.26	289.5
Half-life in water	Not Available	12 – 17 hours	8 hours
Toxicity	Not Available	Rat- LD ₅₀ = 500 mg/kg	Rat- LD ₅₀ =3700 mg/kg
log K _{ow}	-	3.18	4.8

Table S2. LC-MS analysis condition for analysis of naproxen, triclosan and reactive red 180.

Pollutant	Mobile Phase	Flow Rate	Capillary Voltage	Run time
Naproxen	Acetonitrile: 0.5 % Acetic Acid = 60:40	0.3 mL/min	3700 V	30 min
Triclosan	Acetonitrile: 1.0 % Formic Acid = 80:20	0.5 mL/min	4000 V	30 min
Reactive Red 180	Acetonitrile: water = 80:20	0.3 mL/min	4000 V	30 min

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(a) TCS					
Plasma Discharge Time (min)	Avg. % Degradation	% Mineralization	Theoretical Cl⁻ (mg/L)	Observed Cl⁻ (mg/L)	
0	0	0	0	0	
1	91.48	21.60	0.79	0.74	
2	94.76	30.60	1.12	1.12	
4	96.41	48.92	1.80	1.78	
6	99.60	79.59	2.81	2.88	

(b) RR180					
Plasma Discharge Time (min)	Avg. % Degradation	% Mineralization	Theoretical SO₄²⁻ (mg/L)	Observed SO₄²⁻ (mg/L)	
				Liquid	Catalyst
0	0	0	0	0	0
2	37.15	16.09	0.54	0.17	0.30
4	48.51	31.15	1.06	0.58	0.43
8	74.14	48.38	1.64	0.88	0.67
12	80.30	65.82	2.23	1.28	0.85

References

- [1] APHA, ed., 2320 ALKALINITY, in: Stand. Methods Exam. Water Wastewater, 22nd ed., American Public Health Association, Washington DC, 2017. <https://doi.org/doi:10.2105/SMWW.2882.023>.
- [2] 2340 HARDNESS, in: Stand. Methods Exam. Water Wastewater, American Public Health Association, 2017. <https://doi.org/doi:10.2105/SMWW.2882.025>.
- [3] A. Rodrigues, A. Brito, P. Janknecht, M.F. Proena, R. Nogueira, Quantification of humic acids in surface water : effects of divalent cations , pH, and filtration, J. Environ. Monit. 11 (2009) 377–382. <https://doi.org/10.1039/B811942B>.