

Supplementary Material

Response surface optimised photocatalytic degradation and quantitation of repurposed COVID-19 antibiotic pollutants in wastewaters; towards greenness and whiteness perspectives

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Supplementary material

Table 1SM: Reported different photocatalysts used for LEVO, AZI and CEF degradation.

Photocatalysts	Contact time	pH	Degradation %	Source of light	References
LEVO					
ZnO/GO nanoparticles	120 min	9	99.6%	UV light	[25]
Magnetic Ag₃PO₄/rGO/CoFe₂O₄	30 min	3.5-9.4	90.7%	visible light	[34]
Ti/MMO/ZnO	4 hours	9	97.1%	UV light	
W doped BaZrO₃	180 min	10	93.4% under UV and 71.7% under visible light	UV and visible light	[36]
Bi₂O₃/P-C₃N₄	75 min	-	89.2%	Simulated sunlight	[37]
In₂O₃/Ag₂CO₃	90 min	-	86.1%	Xe lamp (300 W)	[38]
AZI					
GO@Fe₃O₄/ZnO/SnO₂ nanocomposite	120 min	3	90.06%	UV light	[26]
ZrO₂/Ag@TiO₂ nanorod composite	8 hours	-	90%	Visible light	[27]
PAC/Fe/Si/Zn Nanocomposite	120 min	8.5	99.7%	UV light	[28]
MoS₂ and MoS₂/GO composites	180 min	-	75 % 87%	xenon lamp	[32]
CEF					
TiO₂ and ZnO Nanoparticles	120 min	6.5	93% 86.7%	UV light	[29]
O₃/UV/Fe₃O₄@TiO₂	30 min		92.4 %	UV light	[35]
AgI/Ag₂WO₄	45 min	-	33%	UV light	[31]
SnS₂/LaFeO₃ composite	150 min	8	87.54%	visible-light-driven photo-Fenton process	[33]
Activated carbon-based TiO₂ composite	100 min	-	99.6%	Led lamp	[39]

Table 2SM. The experiments and results of the Box-Behnken design (BBD)

Run	Coded values			Actual values			Removal % **		
	A	B	C	pH	Np*	Time	LEVO	AZI	CEF
1	+1	+1	0	9	1.0	60	41.1	43.9	46.2
2	+1	-1	0	9	0.2	60	30.3	32.5	34.3
3	0	1	-1	7	1.0	30	51.0	53.3	56.6
4	-1	0	+1	5	0.6	90	70.4	74.4	76.1
5	-1	+1	0	5	1.0	60	44.1	47.0	48.9
6	0	+1	+1	7	1.0	90	90.3	93.1	95.2
7	0	0	0	7	0.6	60	90.9	94.2	97.0
8	0	0	0	7	0.6	60	86.4	84.9	88.1
9	-1	0	-1	5	0.6	30	42.1	44.4	48.4
10	+1	0	-1	9	0.6	30	34.0	37.2	40.1
11	+1	0	+1	9	0.6	90	39.1	42.4	45.2
12	0	-1	-1	7	0.2	30	58.9	61.1	66.3
13	0	0	0	7	0.6	60	88.4	92.2	94.5
14	0	-1	+1	7	0.2	90	70.2	76.8	80.2
15	-1	-1	0	5	0.2	60	45.3	50.0	55.1

* Dose of graphene nitride nanoparticles in g/L.

** Removal % = $(C_0 - C_t) / C_0$ ratio with C_0 and C_t representing the initial and final concentrations.

Table 3SM. BET surface properties and BJH Pore Size Distribution results.

Property	Value
Average Pore Size	1.6 nm
BET Surface area	144.2 m ² /g
Average Particle radius	9.461e+000 nm
Surface Area	15.3 m ² /g
Pore Volume	0.05 cc/g
Pore radius Dv(r)	2.77 nm
Total Pore Volume	0.12 cc/g

Table 4SM. ANOVA of Quadratic model (response 1: removal % of LEVO).

Response 1: Removal % of LEVO						
Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	6714.5	9	746.1	35.7	0.0005	✓
A-pH	406.1	1	406.1	19.5	0.007	✓
B-NP Dose	60.5	1	60.5	2.9	0.1495	X
C-Time	861.1	1	861.1	41.2	0.0014	✓
AB	36.0	1	36.0	1.72	0.2462	X
AC	132.3	1	132.3	6.33	0.0534	X
BC	196.0	1	196.0	9.39	0.028	✓
A ²	4512.3	1	4512.3	216.1	< 0.0001	✓
B ²	693.9	1	693.9	33.2	0.0022	✓
C ²	205.4	1	205.4	9.84	0.0258	✓
Residual	104.4	5	20.9			
Lack of Fit	91.8	3	30.6	4.83	0.176	not significant
Pure Error	12.7	2	6.3			
Cor Total	6818.9	14				

Table 5SM. ANOVA of Quadratic model (response 2: removal % of AZI).

Response 2: Removal % of AZI						
Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	6664.9	9	740.6	26.4	0.0011	✓
A-pH	450.0	1	450.0	16.0	0.0103	✓
B-NP Dose	36.1	1	36.1	1.29	0.3082	X
C-Time	1035.1	1	1035.1	36.9	0.0018	✓
AB	56.6	1	56.3	2.0	0.2161	X
AC	156.3	1	156.3	5.56	0.0648	X
BC	144.0	1	144.0	5.13	0.0729	X
A ²	4373.6	1	4373.6	155.7	< 0.0001	✓
B ²	592.4	1	592.4	21.1	0.0059	✓
C ²	164.1	1	164.1	5.84	0.0603	X
Residual	140.4	5	28.1			
Lack of Fit	95.8	3	31.9	1.43	0.4369	not significant
Pure Error	44.7	2	22.3			
Cor Total	6805.3	14				

Table 6SM. ANOVA of Quadratic model (response 3: removal % of CEF).

Response 3: Removal % of CEF						
Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	6591.4	9	732.4	30.5	0.0008	✓
A-pH	496.1	1	496.1	20.6	0.0062	✓
B-NP Dose	15.1	1	15.1	0.63	0.4637	X
C-Time	924.5	1	924.5	38.4	0.0016	✓
AB	81.0	1	81.0	3.4	0.1259	X
AC	132.3	1	132.3	5.5	0.066	X
BC	156.3	1	156.3	6.5	0.0513	X
A ²	4394.8	1	4394.8	182.7	< 0.0001	✓
B ²	576.9	1	576.9	23.99	0.0045	✓
C ²	144.2	1	144.2	6	0.058	X
Residual	120.3	5	24.1			
Lack of Fit	78.3	3	26.1	1.24	0.4751	not significant
Pure Error	42.0	2	21			
Cor Total	6711.6	14				

Table 7SM. ComplexGAPI metrics

SAMPLE PREPARATION AND ANALYSIS		PRE-ANALYSIS PROCESSES	
Sample preparation		Yield and conditions	
1. Collection:	On-line or at-line ▼	I. Yield:	70-89% ▼
2. Preservation:	None ▼	II. Temperature/time:	Heating, > 1 h Cooling < 0°C ▼
3. Transport:	None ▼	Relation to Green Economy	
4. Storage:	None ▼	III. Number of rules met:	3-4 ▼
5. Type of method:	Extraction required ▼	Reagents and solvents	
6. Scale of extraction:	Nano-extraction ▼	IVa. Health hazard:	Moderately toxic; couli ▼
7. Solvents/reagents used:	Green solvents/reagent ▼	IVb. Safety hazard:	Highest NFPA flammal ▼
8. Additional treatments:	None ▼	Instrumentation	
Reagents and solvents		Va. Technical setup:	Common setup ▼
9. Amount:	10-100 mL (10-100 g) ▼	Vb. Energy:	>1.5 kWh per sample ▼
10. Health hazard:	Moderately toxic; couli ▼	Vc. Occupational hazard:	Hermetization of analy ▼
11. Safety hazard:	Highest NFPA flammal ▼	Workup and purification	
instrumentation		Vla. End products workup, purification:	None or simple proces ▼
12. Energy:	> 1.5 kWh per sample ▼	Vlb. Purity:	97-98% ▼
13. Occupational hazard:	Hermetic sealing of thri ▼	E-factor	
14. Waste:	1-10 mL (1-10 g) ▼	VII. E-factor input:	0.005 <input type="text"/> <input type="button" value="Apply"/>
15. Waste treatment:	No treatment ▼		

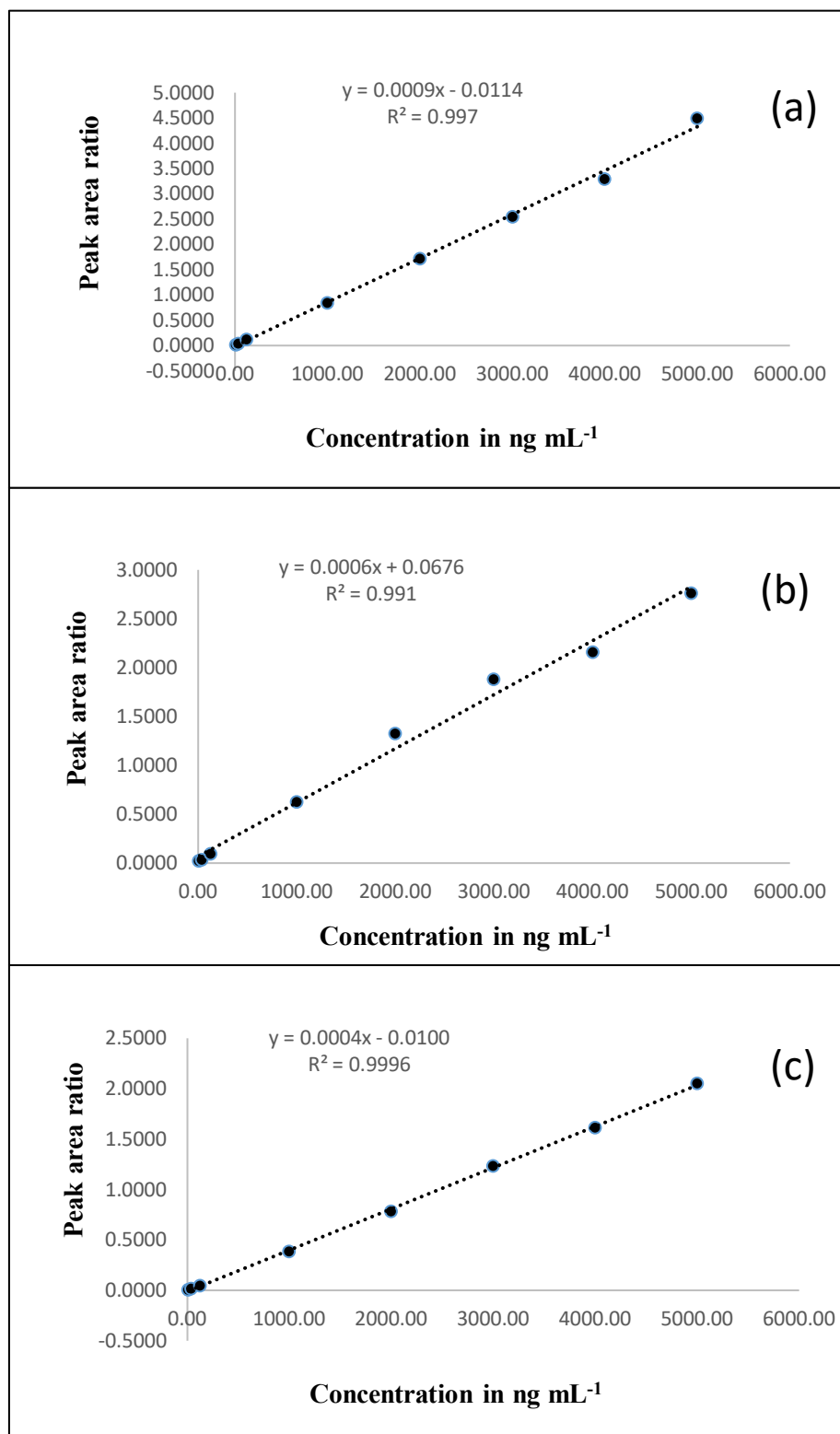


Fig. 1SM. The calibration curve relating the concentration of (a) LEVO, (b) AZI, (c) CEF, in the range of (10-5000 ng/mL) versus the peak area ratio.

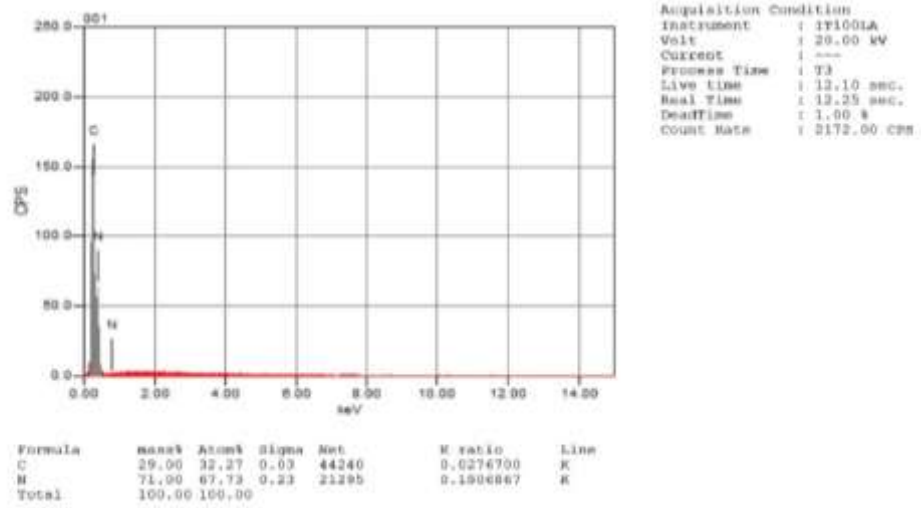
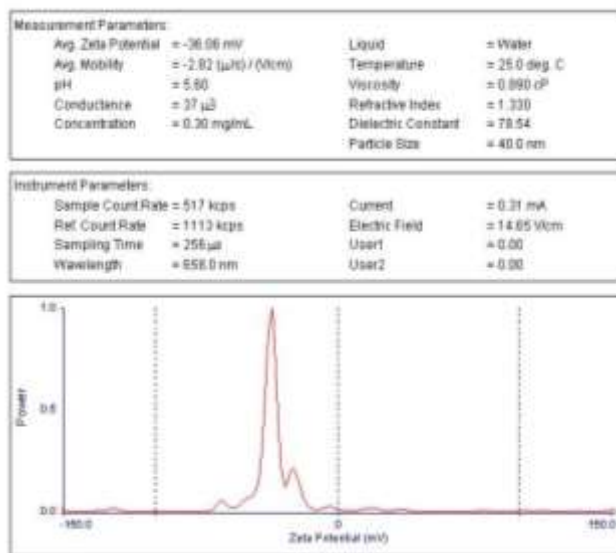
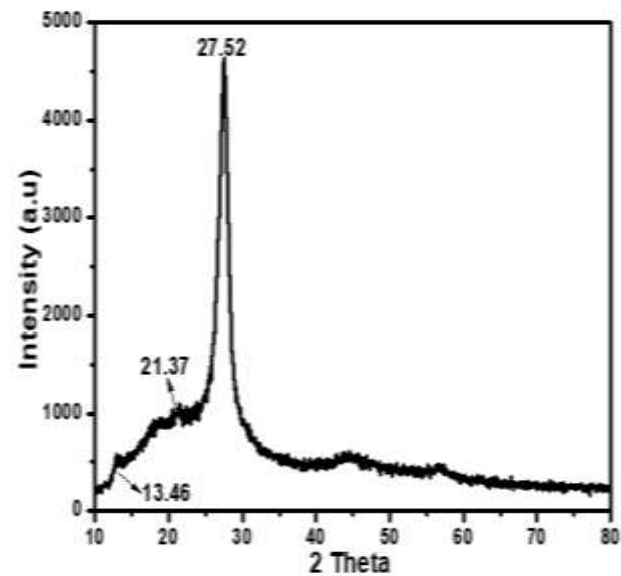


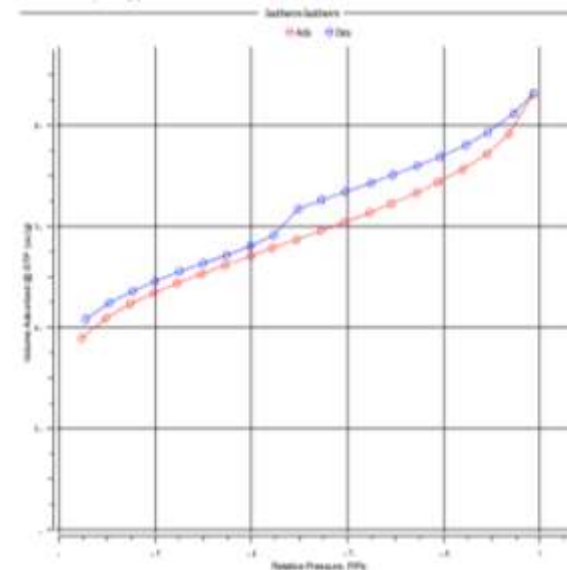
Fig.2SM. The EDX pattern of the synthesized g-C₃N₄.



(a)



(b)



(c)

Fig.3SM (a) Zeta potential of the g-C₃N₄ of -36.06 mV, (b) XRD pattern of g-C₃N₄, (c) The N₂ adsorption-desorption isotherm of g-C₃N₄ and the corresponding pore size distribution curve (inset).

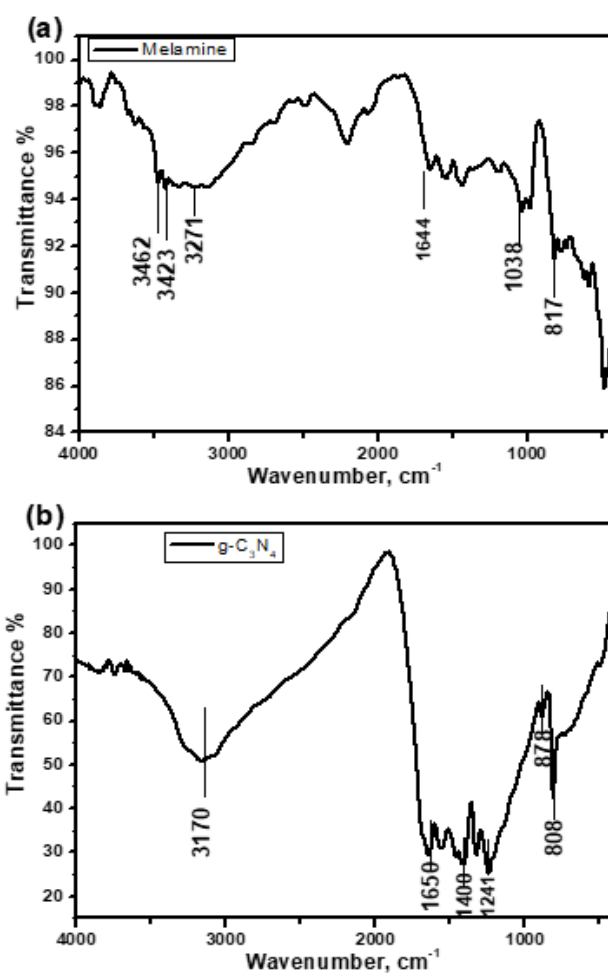


Fig.4SM (a) FTIR spectrum of melamine, (b) FTIR $\text{g-C}_3\text{N}_4$ spectrum.

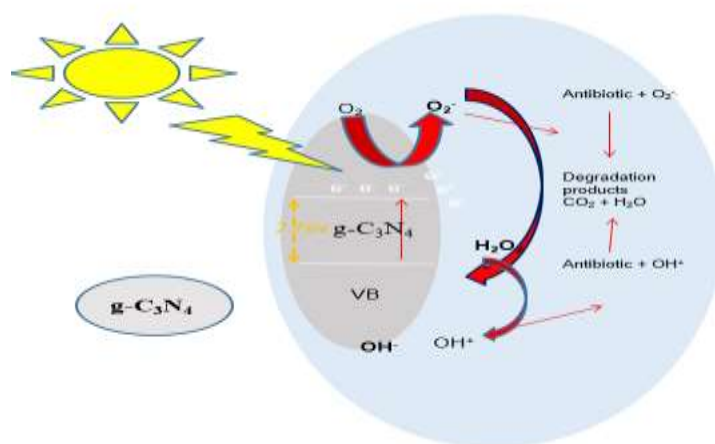


Fig. 5SM. Schematic diagram of degradation mechanism of photocatalyst $\text{g-C}_3\text{N}_4$

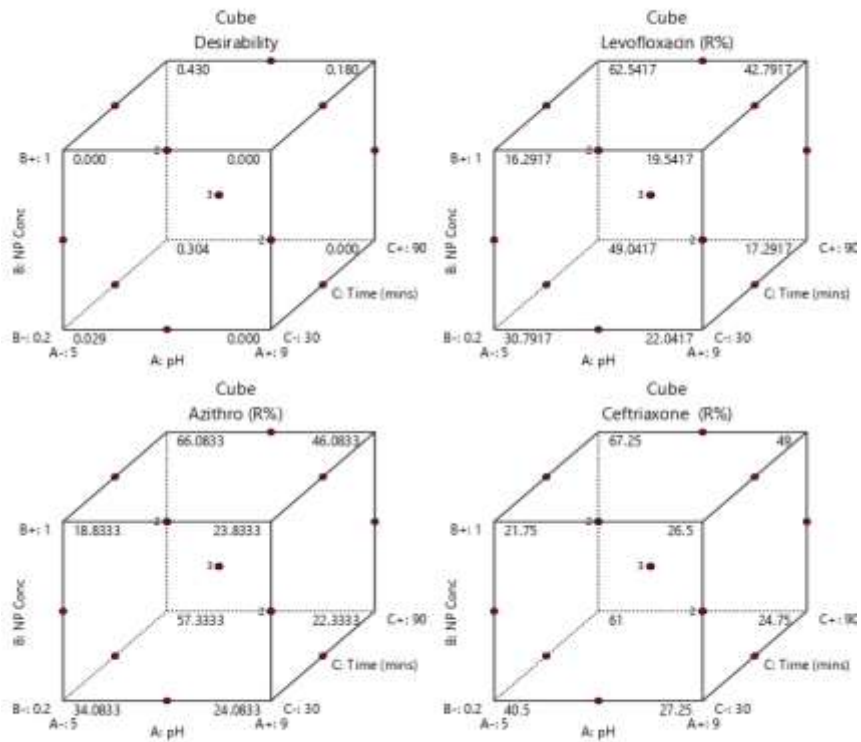


Fig.6SM. 3-D cube plot of Box-Behnken design (BBD) for the significant models for the removal % of LEVO, AZI, and CEF with desirability index (0.886).