Removal of zearalenone mycotoxin with kaolin group-based photocatalysts: Exploration of mechanisms and photodegradation pathways

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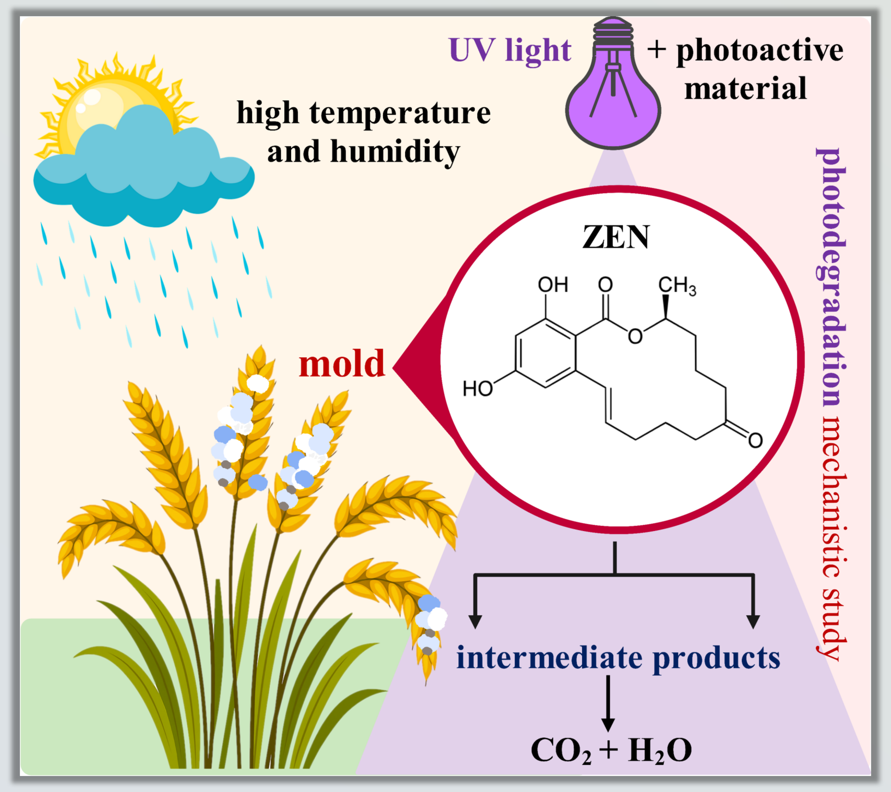
Zearalenone



~25% of global food and agricultural products are contaminated with mycotoxins.

Zearalenone (ZEN)

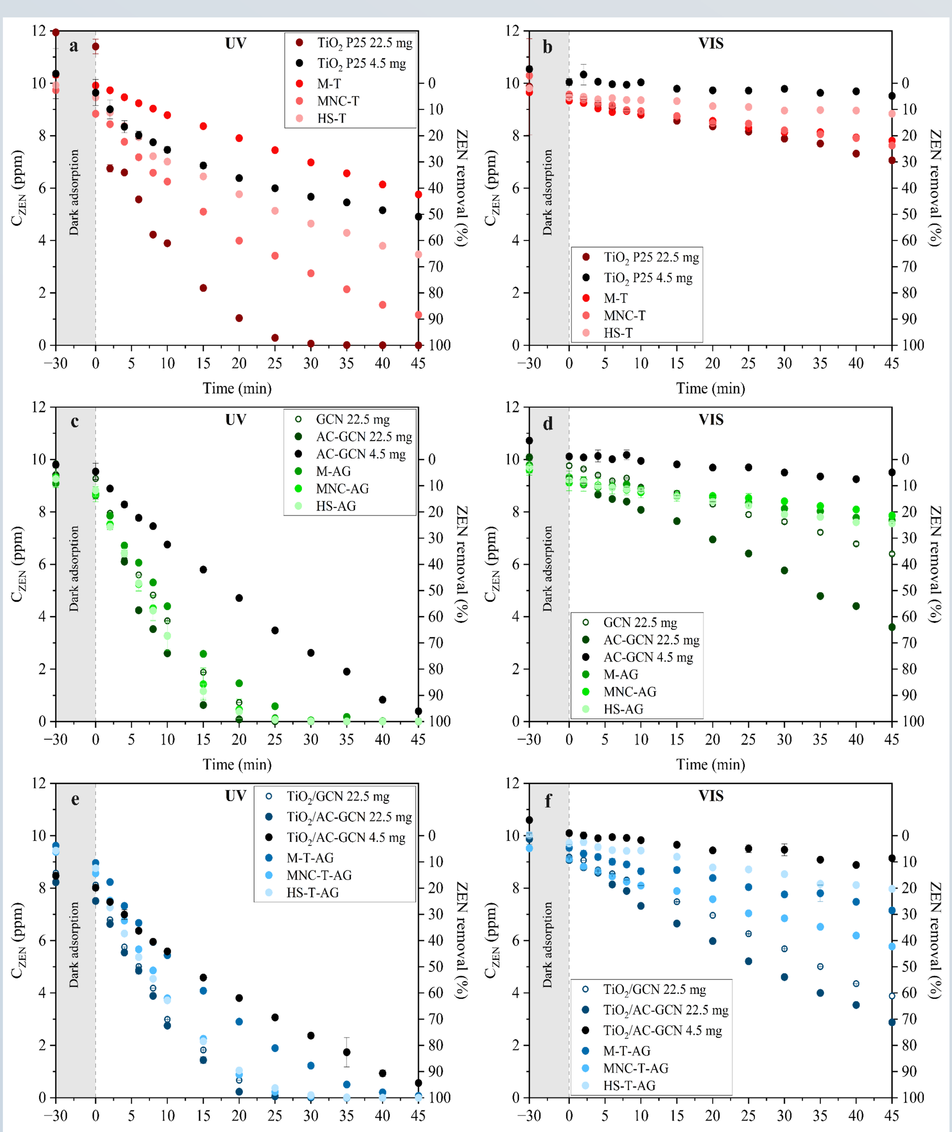
- **One of the most commonly detected mycotoxin.**
- Structure comparable to **natural estrogens.**
- Binds competitively to estrogen receptors in the body.
- Causes enlargement of the uterus, cyst formation, testicular atrophy, reduced sperm concentration, **infertility, miscarriages.**

Materials and their performance

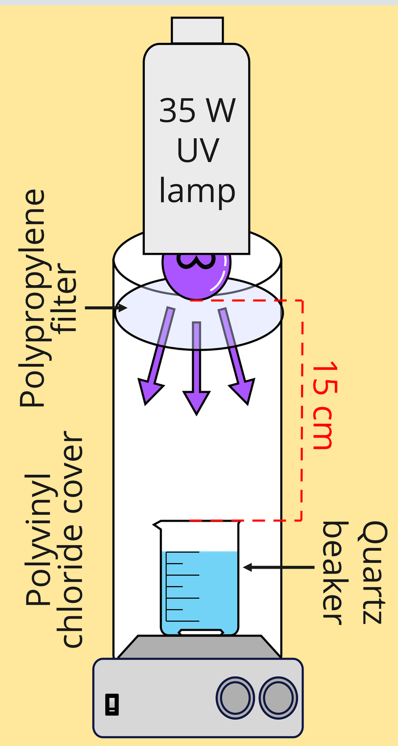
Mineral supports

+ ~20 wt% of semiconductor

Mineral support	TiO_2	g-C_3N_4	TiO_2/g-C_3N_4
M	M-T	M-AG	M-T-AG
HS	HS-T	HS-AG	HS-T-AG
MNC	MNC-T	MNC-AG	MNC-T-AG

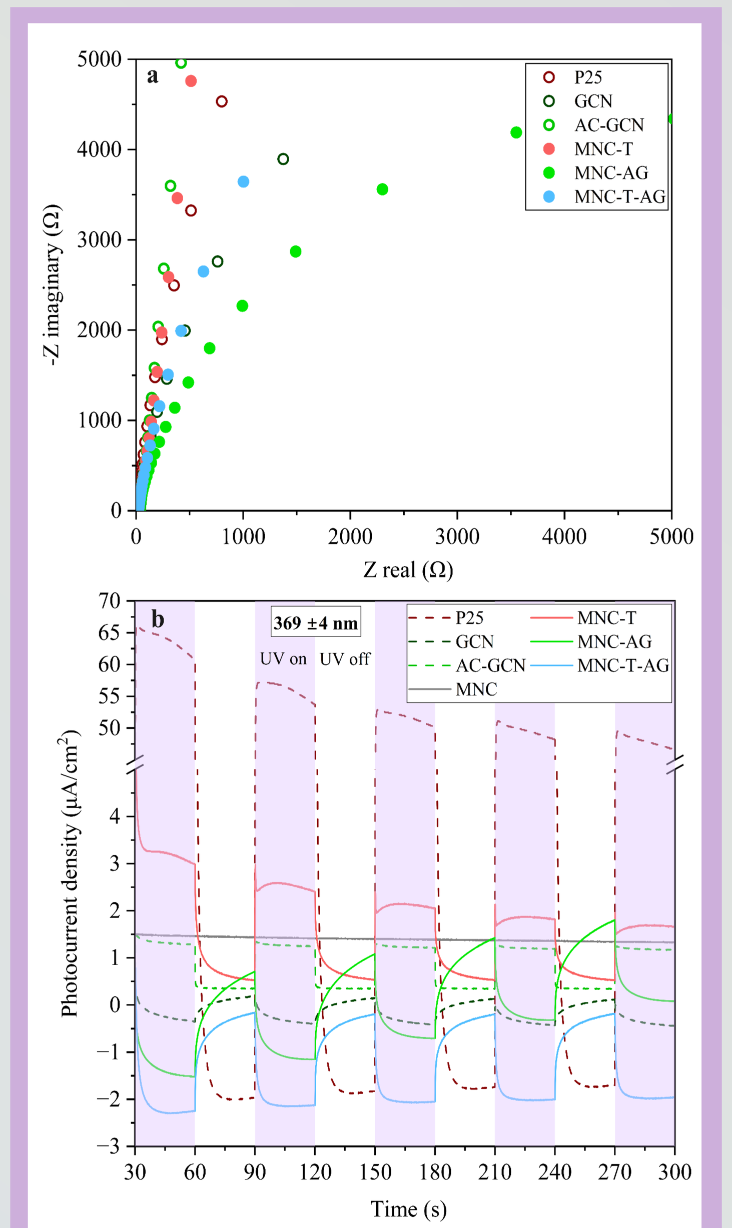


Photodegradation of ZEN using materials containing: (a, b) TiO_2, (c, d) AC-GCN, and (e, f) TiO_2/AC-GCN, under UV light (a, c, e) and visible light irradiation (b, d, f).



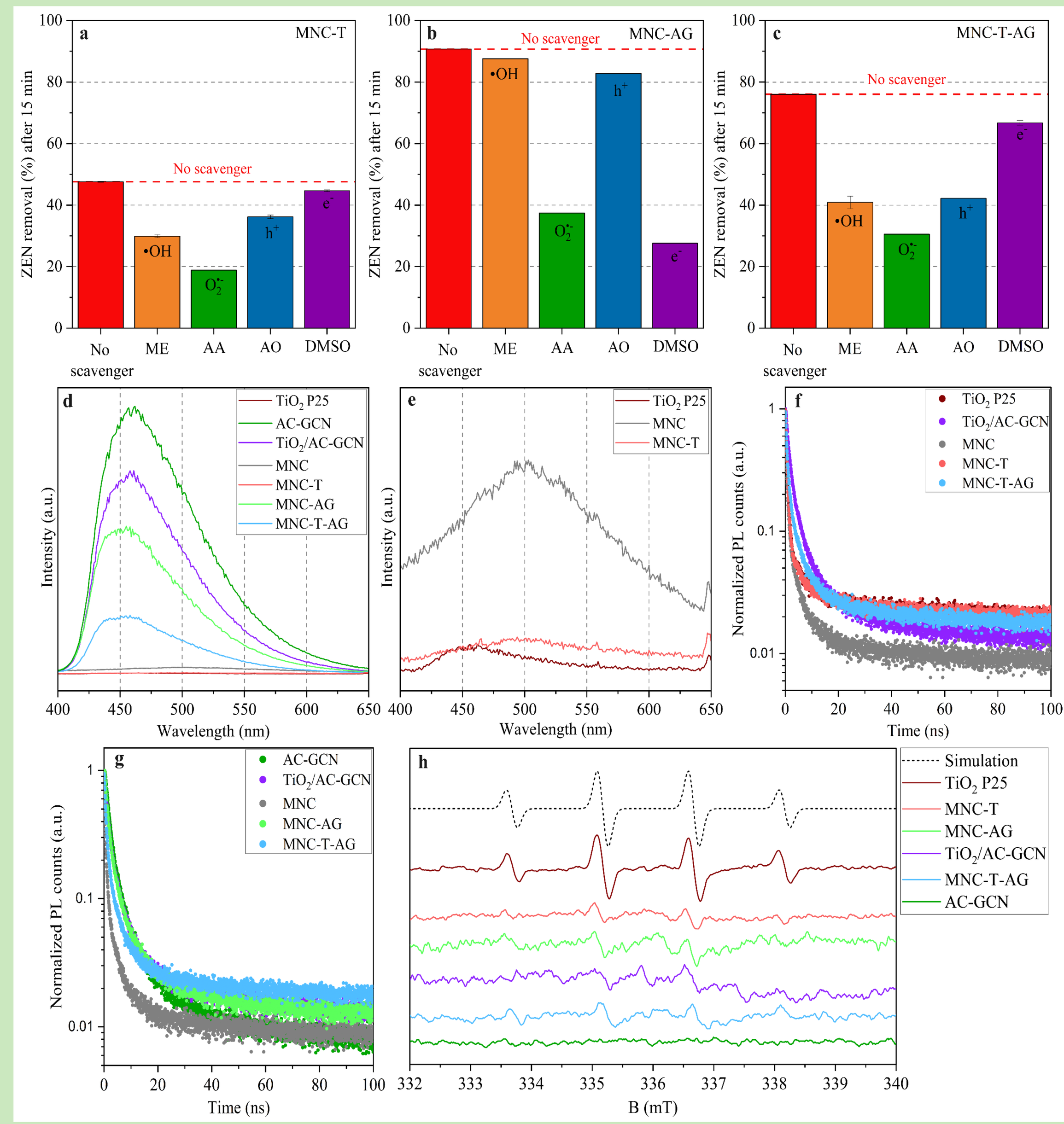
Experimental setup.

Mechanistic study

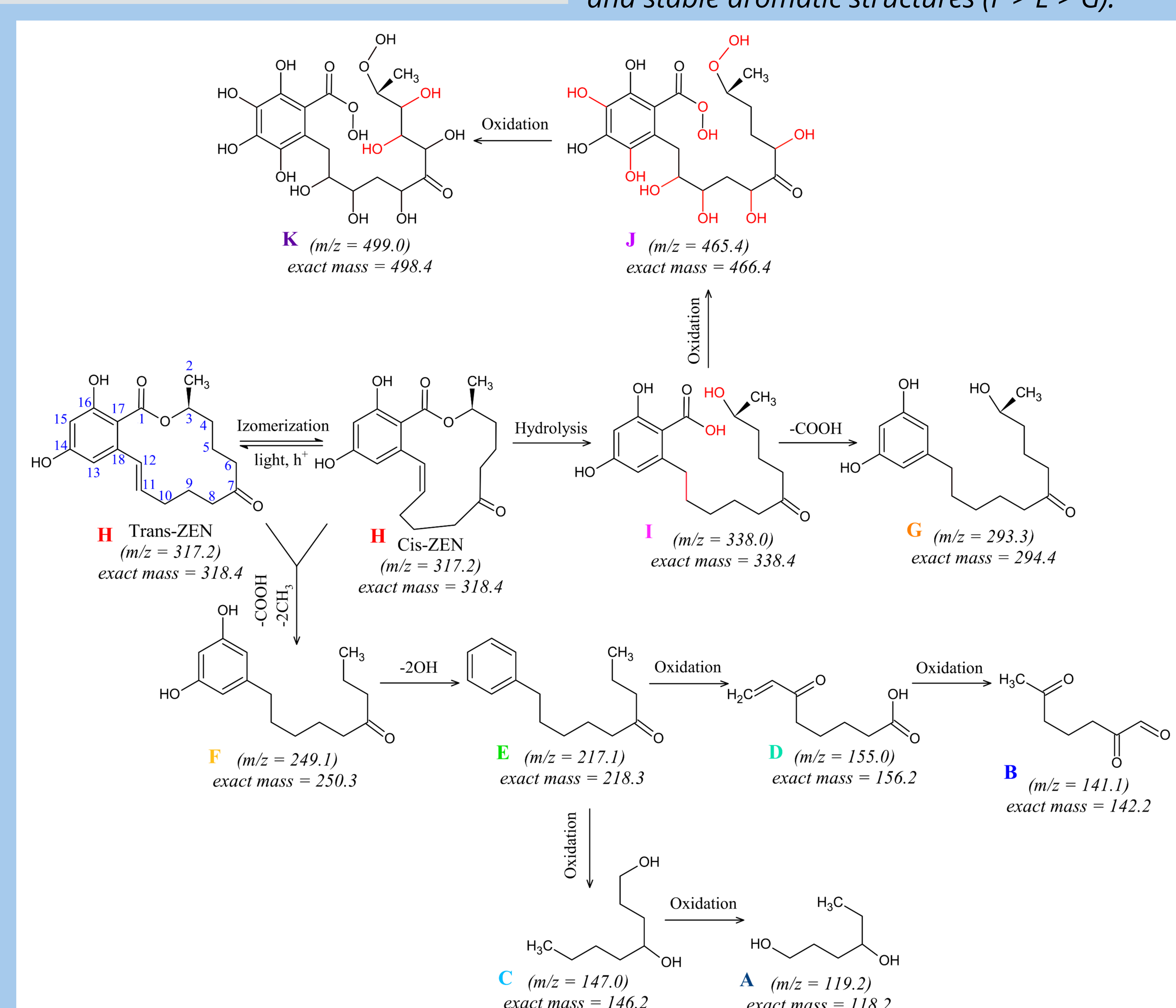


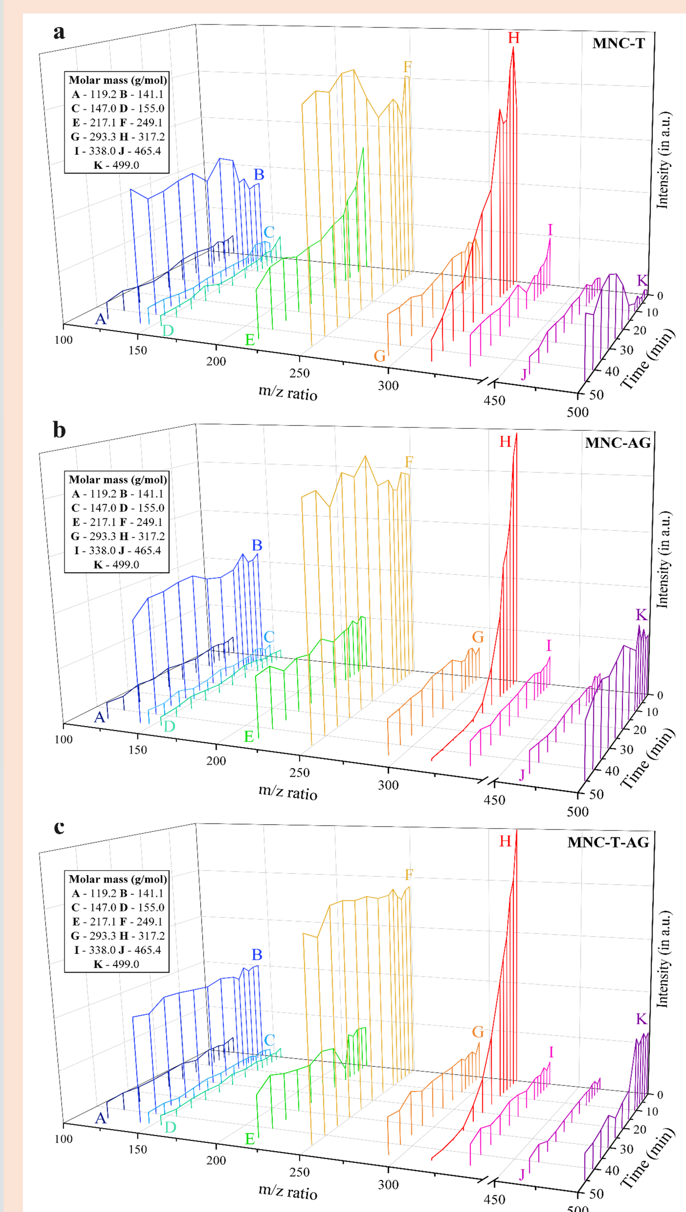
(a) Nyquist plots and (b) transient photocurrent response of the MNC-based composite photocatalysts and control samples.

ZEN removal with (a) MNC-T, (b) MNC-AG, and (c) MNC-T-AG samples in the presence of radical trapping agents; (d) PL spectra of the MNC-based materials with a close-up (e) on MNC, P25 TiO_2, and TiO_2/AC-GCN; (f) TRPL spectra of the MNC-based materials containing TiO_2; (g) TRPL spectra of the MNC-based materials containing AC-GCN and (h) X-band EPR spectra of spin-trapping experiments with DMPO.



Proposed photodegradation pathways of ZEN under UV irradiation. MS analysis showed the dominance of IPs B and F. ZEN photodegradation ultimately leads to simple oxygen-rich chains (B) and stable aromatic structures (F > E > G).





UHPLC-ESI-MS/MS spectra of ZEN and the main intermediate products (IPs) formed in the kinetic photodegradation experiments with (a) MNC-T, (b) MNC-AG, and (c) MNC-T-AG photocatalysts.

IPs hazard category

*Estimated toxicity results for ZEN and the main identified intermediate products (IPs) after photodegradation with the studied photocatalysts, obtained using ECOSAR software.**

m/z	Compound	Molecular formula	Acute toxicity (mg/L)			Chronic toxicity (mg/L)		
			Fish (LC50)	Daphnid (LC50)	Algae (EC50)	Fish (ChV)	Daphnid (ChV)	Algae (ChV)
499.0	K	$C_{18}H_{26}O_{16}$	4.21	15.7	15.7	0.90	46.5	52.9
495.4	J	$C_{18}H_{26}O_{14}$	2.18	5.75	6.62	0.33	11.7	18.0
338.0	I	$C_{18}H_{26}O_6$	54.4	301	35.8	26.2	107	5.45
317.2	ZEN	$C_{18}H_{22}O_5$	1.95	8.13	1.95	0.84	2.76	0.33
293.3	G	$C_{17}H_{26}O_4$	4.57	25.0	3.05	2.19	8.86	0.47
249.1	F	$C_{15}H_{22}O_3$	1.81	7.95	1.68	0.799	2.72	0.28
217.1	E	$C_{15}H_{22}O$	1.20	0.86	1.60	0.153	0.16	0.69
155.0	D	$C_8H_{12}O_3$	1.92E+3	1.29E+3	3.79E+3	3.41E+3	92.2	136
147.0	C	$C_8H_{18}O_2$	236	130	85.5	22.3	11.7	20.9
141.1	B	$C_7H_{10}O_3$	444	571	225	376	3.23	50.2
119.2	A	$C_6H_{14}O_2$	1.45E+3	731	331	123	51.0	66.2

*To determine the appropriate hazard category of the compounds, the lowest acute toxicity values within and between different trophic levels (fish, daphnid, and algae) were used.

White boxes, not harmful: LC50/EC50/ChV > 100
blue boxes, harmful: 100 ≥ LC50/EC50/ChV > 10
green boxes, toxic: 10 ≥ LC50/EC50/ChV > 1
yellow boxes, very toxic: LC50/EC50/ChV ≤ 1

Conclusions

- Kaolinite nanotubes combined with GCN and the TiO_2/GCN mixture achieved **the highest ZEN removal efficiencies - 98.8% and 97.7%,** respectively - after 25 min of UV irradiation from an initial concentration of 10 ppm.
- Scavenger experiments and EPR measurements **identified $O_2^{\bullet-}$ and •OH radicals as the key reactive species** responsible for ZEN photodegradation.
- TRPL measurements demonstrated **prolonged charge carrier lifetimes** in materials containing kaolinite nanotubes and GCN.
- CLV confirmed **the presence of charge traps** in the photocatalyst structure, contributing to improved performance.
- The proposed ZEN degradation pathways involved **hydrolysis, oxidation, and cleavage reactions**, resulting in intermediate products with both lower and higher molecular weights.

WEBSITE **ARTICLE** **ABSTRACT**

Chemical Engineering Journal

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