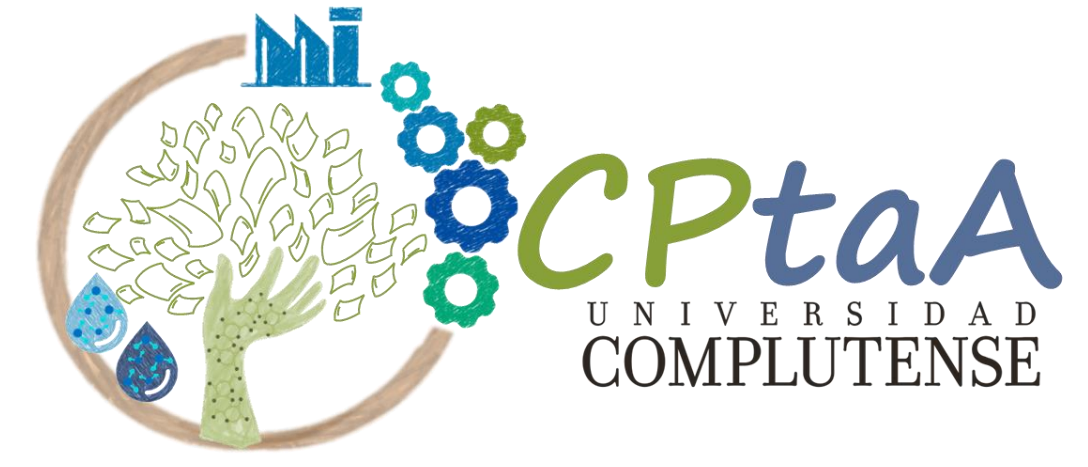


QUATERNARY TREATMENTS FOR THE REMOVAL OF PHARMACEUTICAL MICROPOLLUTANTS (MPs) IN WASTEWATER UNDER EU REGULATORY FRAMEWORK



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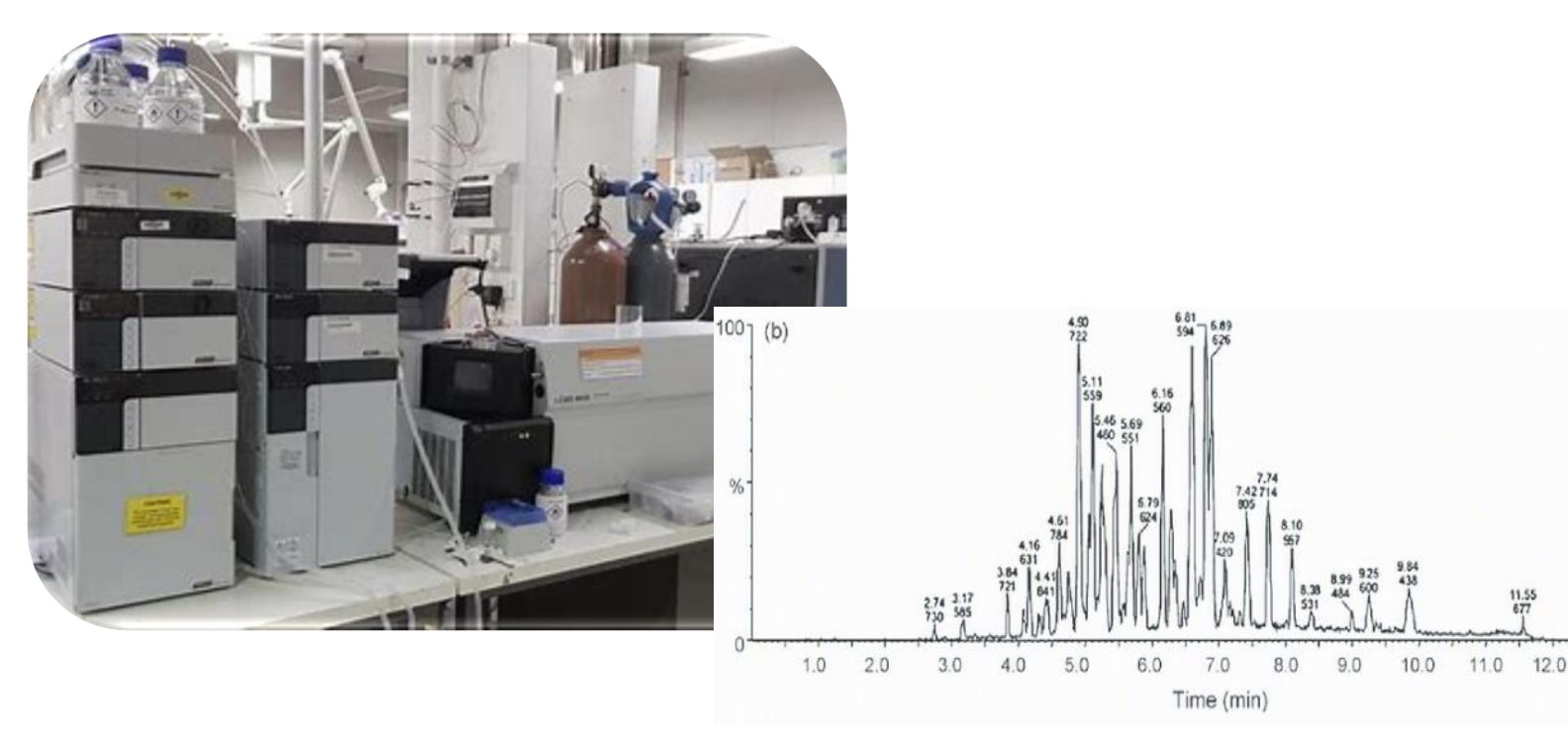
Major Challenge in WWTPs → MPs in effluents → EU 2024/3019 Directive → Mandatory quaternary treatment for MP removal
Ozonation and Activated Carbon Adsorption: Performance depends on MP physicochemical properties

WASTEWATER MATRIX



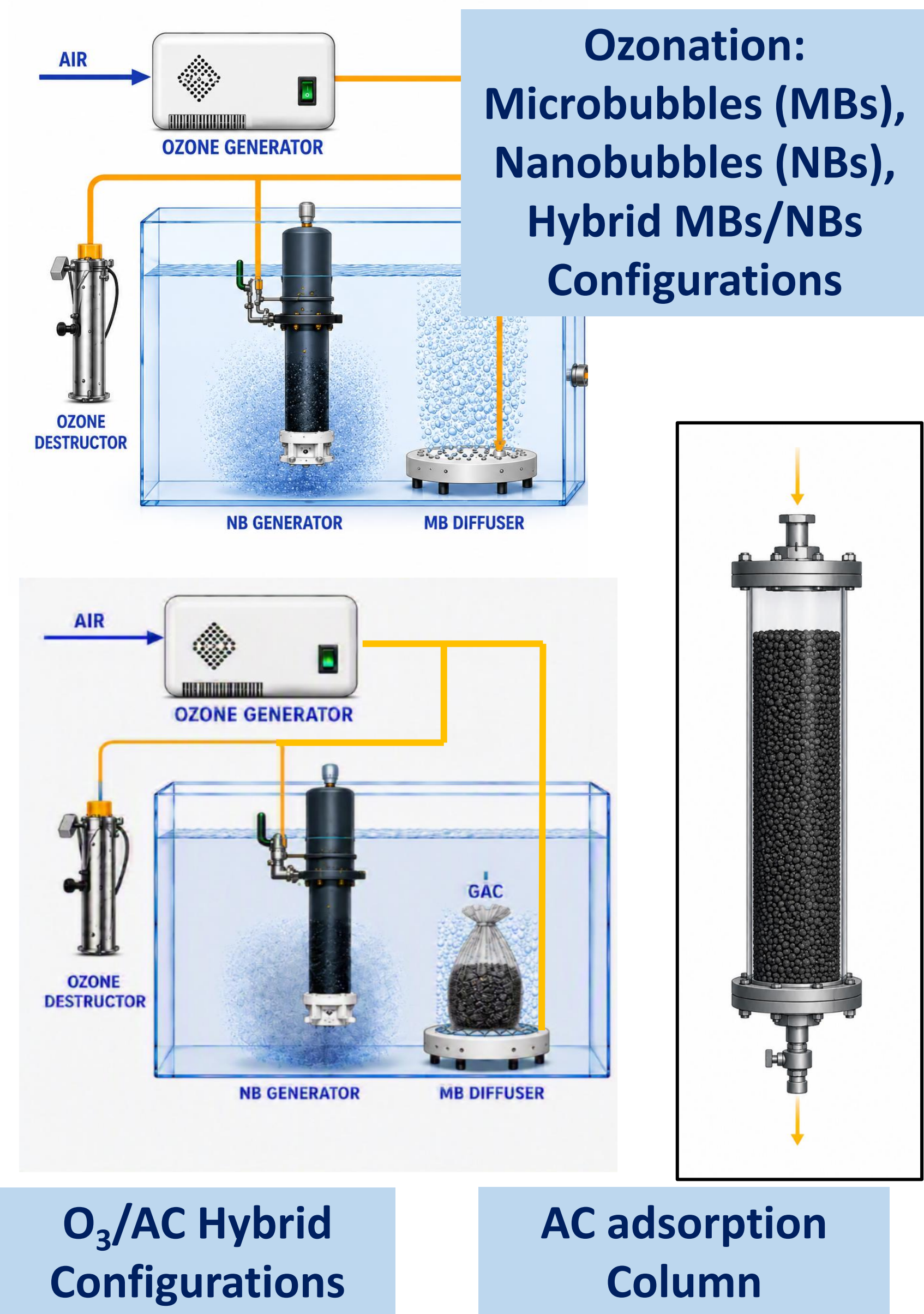
Tertiary urban WWTP effluent+ 15 Pharmaceutical MPs

MP CHARACTERIZATION



LC-QQQ-MS. LC8030 (Shimadzu)

QUATERNARY TECHNOLOGIES



PREDICTIVE FRAMEWORK

ACAR - Activated Carbon Adsorption Rank

Mechanistic descriptors

- Hydrophobic Adsorption Potential (AC1)
- π - π Interaction Potential (AC2)
- Hydration and Water Competition (AC3)
- Micropore Accessibility (AC4)
- Basicity Correction Term (AC5)



Predicted adsorption potential

$$ACAR = AC1 + AC2 - AC3 - AC4 + AC5$$

IRO₃ - Index of Reactivity toward Ozone

Mechanistic descriptors

- Direct Ozone Reactivity (O1)
- Electronic Activation of Aromatic Systems (O2)
- Structural Stability (O3)
- Structural Accessibility (O4)
- Radical Pathway Contribution (O5)
- Post-oxidation Fragmentation Potential (O6)



Predicted ozonation susceptibility

$$IRO_3 = \alpha \cdot O1 + \beta \cdot O2 - \gamma \cdot O3 + \delta \cdot O4 + \varepsilon \cdot O5 + \zeta \cdot O6$$

Results

PREDICTIVE FRAMEWORK

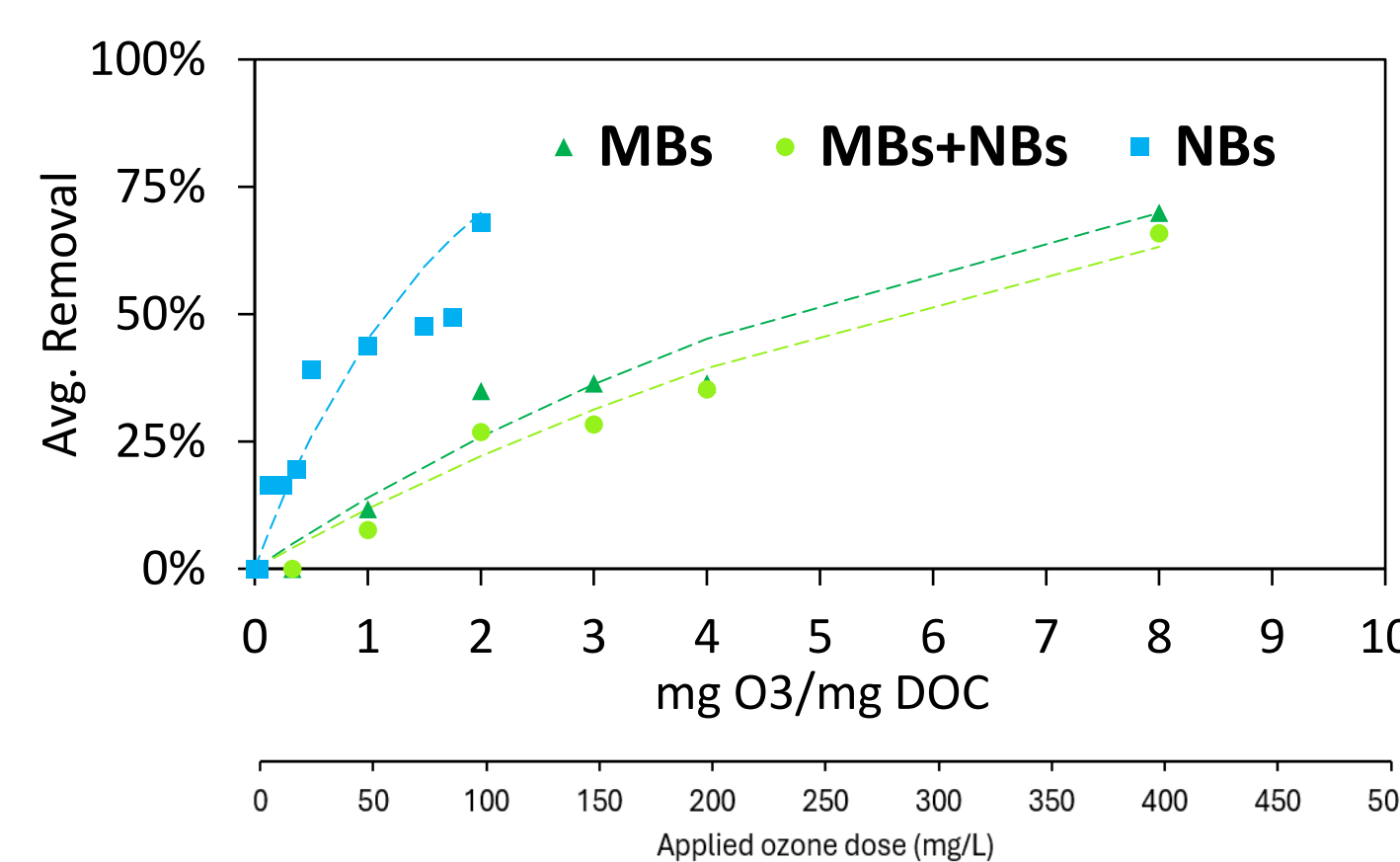
Compound	Type	Predicted ozonation (IRO ₃)						Predicted adsorption potential (ACAR)					
		O1	O2	O3	O4	O5	O6	AC1	AC2	AC3	AC4	AC5	ACAR
Etoposide	Anticancer (topoisomerase inhibitor)												0.0
Mycophenolic Acid	Immuno-suppressant												1.8
Tylosin	Macrolide antibiotic												0.6
Tetracycline	Antibiotic												-1.4
Bisphenol A	Plastic monomer, endocrine disruptor												3.9
Clarithromycin	Macrolide												1.4
Naproxen	Nonsteroidal anti-inflammatory drug (NSAID)												2.6
Prednisone	Corticosteroid												-0.2
Estradiol (α/β)	Sex hormone (estrogen)												3.1
5-Fluorouracil	Antimetabolite (anticancer)												-1.0
Diclofenac	NSAID, Anti-inflammatory, analgesic												3.4
Venlafaxine	SNRI antidepressant												3.0
Methotrexate	Antimetabolite (anticancer)												-2.4
Tamoxifen	Endocrine therapy (anti-estrogen)												4.2
Irbesartan	Angiotensin II receptor blocker (ARB)												2.5
Ketoconazole	Azole antifungal												4.3
5-Methylbenzotriazole	Corrosion inhibitor												1.6
Benzotriazole	Triazole (corrosion inhibitor)												1.3
Amiodarone	Antiarrhythmic												4.5
Bicalutamide	Non-steroidal anti-androgen												2.1
Flutamide	Non-steroidal anti-androgen												1.1

QUATERNARY TECHNOLOGIES

Ozonation Removal of 15 cytostatics

General Conditions

- MBs vs MBs/NBs vs NBs
- Treated wastewater per run: 5L
- 50 mg/L DOC
- MP concentration: 25 µg/L

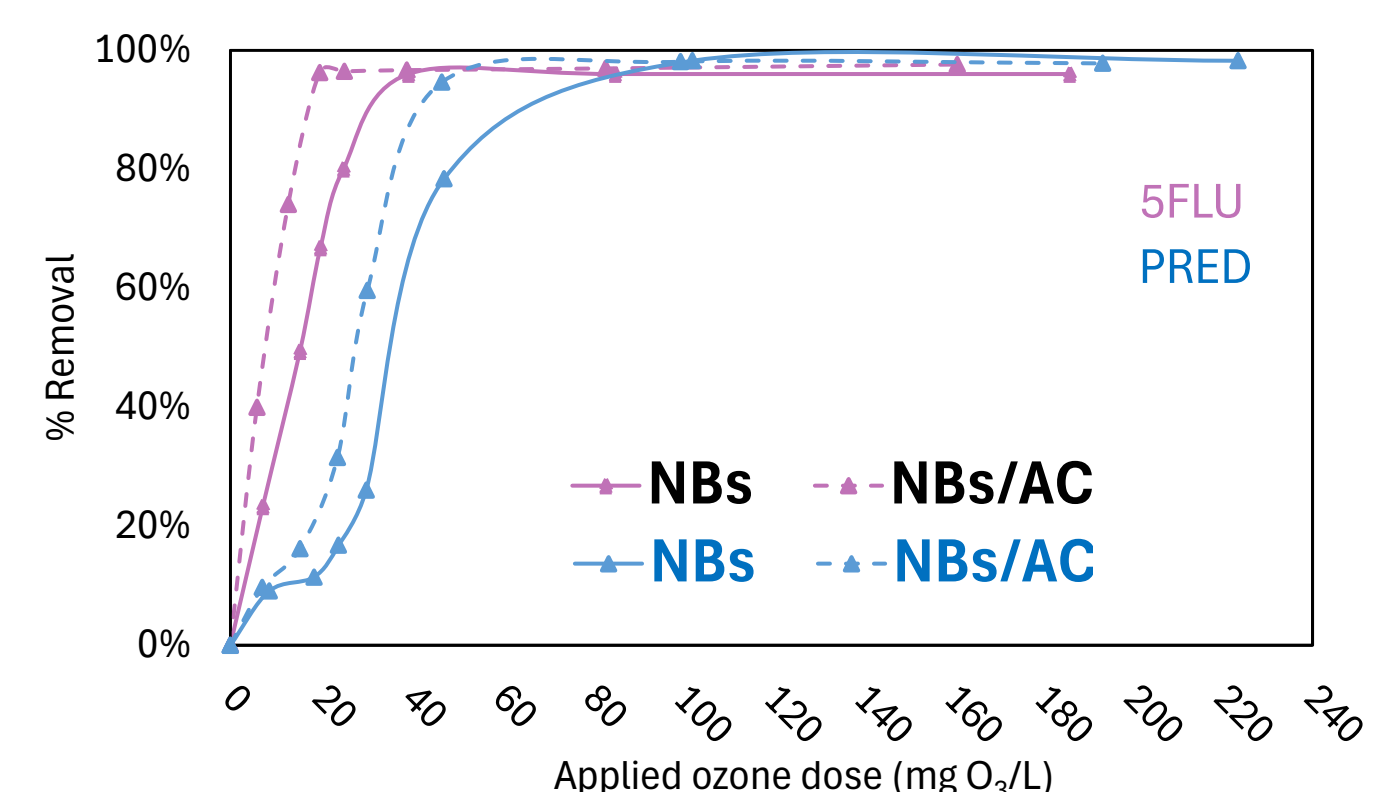


NBs significantly enhanced ozonation efficiency compared with conventional MB treatments

Hybrid NB Ozonation + AC Adsorption

General Conditions

- AC: 10 g · 0.5 $\frac{gO_3}{gDOC}$
- Treated water per run: 5 L
- 5-FLU or PRED concentration: 20 mg/L



As predicted by IRO₃, both pharmaceuticals showed high susceptibility to ozonation. In contrast, ACAR correctly predicted the limited contribution of AC to the final removal

Conclusions

- The predictive frameworks, IRO₃ for ozonation and ACAR for AC adsorption, constitute useful screening tools to support the selection of quaternary treatments based on the pharmaceutical micropollutant structure.
- NB-assisted ozonation achieved high removal efficiency with >85% ozone savings, demonstrating a substantial process intensification.
- Hybrid NB-O₃/AC hybrid configurations enable a dual treatment with synergic effects to target a higher number of pharmaceutical MPs.

Acknowledgments

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