FROM COMPLEX MULTIFUNCTIONAL ARCHITECTURES TO PRACTICAL SOLUTIONS FOR WATER REMEDIATION

Miriam Abán[†], Sara Rojas[*] and Patricia Horcajada[†]
[†]*Advanced Porous Materials Unit, IMDEA Energy, Móstoles,28935, Spain*
[*]*Department of Inorganic Chemistry, University of Granada, Granada, 18071, Spain*

Our view of the present state of research

Emerging contaminants (ECs) comprise a chemically diverse group of unregulated contaminants detected in water, soil, air, food, and even in humans. They originate from industrial and agricultural processes, as well as from everyday human activities, and include pesticides, per- and polyfluoroalkyl substances (PFAS), microplastics, metal ions, pharmaceuticals, and personal care products (PCPPs), among others. Although normally these species are present in trace/safe concentrations in water bodies, the simultaneous occurrence of multiple ECs, together with their bioaccumulative and persistent nature, poses potential long-term harm to both ecosystems and human health. Conventional wastewater treatment plants (WWTPs) are not prepared to remove these contaminants, as they are found in the water effluents, mainly due to their low concentrations, chemical complexity and the lack of suitable detection and removal technologies, highlighting the need for alternative solutions [1].

Among the technologies investigated for the removal of ECs, adsorption, membrane filtration, biological treatments and advanced oxidation processes (AOPs) are the most widely used [2]. More recently, metal-organic frameworks (MOFs) have emerged as versatile multifunctional materials for water remediation. Their fundamentally higher level of complexity-arising from the combination of inorganic nodes and organic linkers, together with their crystalline “a la carte” design, exceptional sorption capacities, and tunable cavities, makes them particularly attractive candidates. MOFs are able to integrate various functions (*e.g.*, adsorption, catalysis, disinfection, sustained and synergistic release) [3] in a single MOF structure or within more complex systems (*e.g.*, enzyme-, polymer-, metal-, metal oxide-, carbonaceous materials-MOF) [4,5], and can also be processed as practical devices (*e.g.*, membranes, packed columns) [6] for water treatment. Such versatility offers a promising pathway to overcome the limitations of conventional methods, an opportunity that our research is actively exploring.

Our recent research contributions in water remediation: from multifunctional complexity to practical simplicity

Harnessing this potential, our research has focused on the design and application of MOF-based systems for environmental remediation, with a particular focus on emerging organic contaminants (EOCs). We approach this challenge from two complementary angles: i) the removal of EOCs already present in waters; and ii) the mitigation of their release into de environment.

First, we focused on the removal of PPCPs, which are among the most persistent and widespread contaminants detected in water sources. Since the pioneer reports on PPCPs adsorption [7] and degradation [8] using MOFs, our research has significantly advanced the field towards more realistic conditions by addressing critical yet often-overlooked aspects such as material stability, regeneration, recyclability, and long-term operation in complex matrices (*e.g.*, tap water) under continuous flow. In this context, the use of more complex MOF architectures has been particularly impactful: defect-engineered frameworks have shown enhanced adsorption capacities and prolonged operation [9], while Ag@MOF composites enabled the first demonstration of continuous-flow photodegradation of contaminants [10] and even exhibit complementary intrinsic disinfection properties [11]. Further advances include the simultaneous degradation of multiple pollutants [12], and the integration of adsorption and photodegradation within a single MOF, leading to more efficient and versatile water treatment [13]. Building upon these developments, we have also validated MOF performance under complex realistic conditions. Using wastewater from urban WWTPs, in collaboration with Inge's group, we demonstrated the high efficiency of a Zr-ellagate MOF, which removed 9 out of 17 detected pharmaceuticals under batch conditions [14]. More recently, a Bi-ellagate MOF was tested at pilot scale, achieving the elimination of 8 out of 14 monitored contaminants over 80 consecutive cycles, thereby demonstrating both efficiency and robustness under operationally relevant conditions [15].

Beyond pharmaceutical contaminants, we have pioneered the degradation of microplastics at room temperature using MOFs. For this purpose, we developed a composite based on the enzyme Candida rugosa immobilized on the outer surface of a Zr-MOF. Remarkably, the biocomposite was able not only to degrade polyethylene terephthalate (PET) derived from a common plastic bottle, but also to further break down its primary degradation product (*i.e.*, bis(2-hydroxyethyl) terephthalate, BHET) into the final terephthalate product (*i.e.*, >37% degradation in 24 h). It is important to note that it maintained good stability and recyclability with minimal enzyme leaching, being also able to adsorb the toxic plastic degradation by-products, as well as other contaminants [16].

Beyond PPCPs and plastics, attention must also be given to potentially toxic by-products formed during water disinfection process. For instance, the use of chlorine dioxide generates chlorites and chlorates, which may be harmful at high concentrations. We demonstrated that a biocompatible, flexible iron MOF efficiently removed these oxyanions, operating continuously for 3 days and, after simple NaCl regeneration, reaching a total lifetime of 6.4 days under drinking water treatment plant (DWTP) conditions [17,18]. Altogether, these advances illustrate how tailored, multifunctional materials can translate into simple, practical solutions for water treatment under real-world conditions. (*i.e.*, 100% ClO_2^- in only 1 min and 30% ClO_3^- in 5 min).

At this point, we believe that our research group, along with others [3,5,19], has demonstrated the potential of MOFs in water treatment. Seeking to go further, we explored their role in contaminant prevention, originally proposing a second strategy: the use of ECs as linkers in MOF construction. Particularly, we developed AgroMOFs, built from agrochemicals as constitutive linkers and active metal cations, and studied them as controlled release agents. AgroMOFs ensure high active loadings, avoid multi-step post-synthetic procedures, are economically attractive, and enable slow, degradation-driven release, minimizing harmful agrochemical peaks in the environment. The first reported AgroMOF, based on the herbicide glufosinate and Cu^{2+} [20], demonstrated a superior activity and selective herbicidal effect while remianing safe for crops. This highlights the potential of combining herbicide and antibacterial/antifungal units within AgroMOFs to generate multifunctional agrochemicals. Building on this approach, we developed a Mg-fosfomycin (antibacterial) MOF with a prolonged two-step Mg^{2+} release and enhanced fertilizer effect compared to the typically used $Mg(SO_4)_2$ [21]. In addition, porous MOFs, intrinsically active or not, can also act as hosts as carriers or coatings for active compounds (*e.g.*, the fertilizer hydroxyapatite) [22], enabling sustained and localized release.

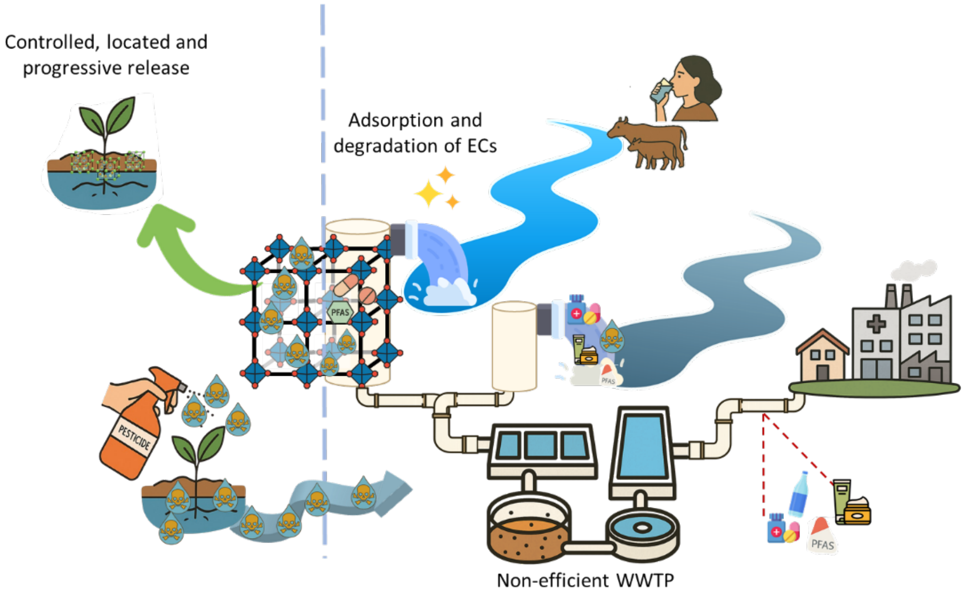

Figure 1. Scheme of application of MOFs in water decontamination

Outlook for future developments

Although multifunctional MOFs have demonstrated remarkable potential for water remediation, several challenges need to be addressed before their large-scale implementation is viable. Emphasis needs to be placed on real-world applicability, moving beyond idealized laboratory conditions to explore material stability, recyclability, continuous-flow operation, and performance in real wastewaters.

Key limitations include: i) the scalability and cost of synthesis, particularly for frameworks incorporating complex or expensive linkers, ii) the long-term environmental stability under harsh and fluctuating conditions (pH, salinity, organic matter), and iii) the risk of metal or ligand leaching, which demands thorough toxicological evaluation. Integration into existing WWTPs remains particularly complex, requiring operational robustness and regulatory approval. However, implementation could be more straightforward in smaller-scale systems (*e.g.*, water filter carafes) or in specific contaminated settings (*e.g.*, hospitals, industry), thus opening more tangible opportunities in these areas

Given these limitations, future efforts should focus on developing more environmentally friendly and scalable synthetic routes using abundant, low-cost precursors, considering life-cycle and techno-economic assessments. In addition, research into hybrid systems combining MOFs with membranes, enzymes, or other adsorbents/catalysts, among others, could enhance selectivity and resilience. However, this complexity must remain balanced with simplicity and scalability to ensure practical applicability in water treatment. Finally, the rational design of AgroMOFs offers a promising strategy to unify environmental protection and sustainable agriculture.

Acknowledgments

The authors acknowledged the financial support of ESENCE (RTC2019-007254-5), MOFSEIDON (PID2019-104228RB-100 MCI/AEI/FEDER, UE), AgroMOF projects (TED2021-132440B-I00 MCI/AEI/FEDER, UE) and CMOFs4water-CM project from Comunidad de Madrid (TEC-2024/ECO-332). M.A. and P.H. acknowledge support from “Comunidad de Madrid” via a predoctoral grant (PIPF-2022/BIO-24064).

References

1. X. Li, X. Shen, W. Jiang, Y. Xi, S. Li, *Ecotoxicol. Environ. Saf.* **278**, 116420 (2024).
2. A. Thirunavukkarasu, R. Nithya, R. Sivashankar, *Rev. Environ. Sci. Biotechnol.* **19**, 751 (2020).
3. F. Yang, M. Du, K. Yin, Z. Qiu, J. Zhao *et. al.*, *Small* **18**, 2105715 (2022).
4. J. Wang, Y. Zhao, R. Peng, Y. Wang, J. Zhang *et. al.*, *Chem. Eng. J* **466**, 142993 (2023).

5. J.-Q. Chen, Z. Sharifzadeh, F. Bigdeli, S. Gholizadeh, Z. Li, *et. al.*, *J. Environ. Chem. Eng*. **11**, 109469 (2023).
6. M. Ghomi, *Mater. Chem. Horizons* **3**, 1078 (2024).
7. E. Haque, J. E. Lee, I. T. Jang, Y. K. Hwang, J.-S. Chang *et al.*, *J. Hazard. Mater*. **181**, 535 (2010).
8. M. Alvaro, E. Carbonell, B. Ferrer, F. X. Llabrés i Xamena, H. Garcia, *Chem. Eur. J.* **13**, 5106 (2007).
9. S. Rojas, J. A. R. Navarro, P. Horcajada, *Dalton Trans*. **50**, 2493 (2021).
10. A. Arenas-Vivo, S. Rojas, I. Ocaña, A. Torres, M. Liras *et al.*, *J. Mater. Chem. A* **9**, 15704 (2021).
11. A. Arenas-Vivo, G. Amariei, S. Aguado, R. Rosal, P. Horcajada, *Acta Biomater*. **97**, 490 (2019).
12. S. Rojas, J. García-González, P. Salcedo-Abraira, I. Rincón, J. Castells-Gil *et al.*, *Sci. Rep.* **12**, 1 (2022).
13. A. J. Chacón-García, S. Rojas, E. S. Grape, F. Salles, T. Willhammar *et al., Sci. Rep.* **14**, 1 (2024).
14. E. S. Grape, A. J. Chacón-García, S. Rojas, Y. Pérez, A. Jaworski *et al., Nat. Water* **1**, 433 (2023).
15. I. Rincon, F. Salles, M. Bofí, M. C. Beneitez, M. E. Gil-Alegre, *et. al.*, 2025, submitted.
16. I. Rincón, T. Hidalgo, G. Armani, S. Rojas, P. Horcajada, *ChemSusChem* **17**, 1 (2024).
17. G. Sanchez-Cano, P. Cristobal-Cueto, P. Nuño-Ortega, L. Sáez, A. Lastra *et al.*, J. *Environ. Chem. Eng*. **12**, 112131 (2024).
18. G. Sanchez-Cano, P. Cristobal-Cueto, L. Sáez, A. Lastra, A. Martín-Calvo *et al.*, *Chem* **11**, 1 (2025).
19. S. Rojas, P. Horcajada, *Chem. Rev*. **120**, 8378 (2020).
20. B. Sierra-Serrano, A. García-García, T. Hidalgo, D. Ruiz-Camino, A. Rodríguez-Diéguez *et al.*, *ACS Appl. Mater. Interfaces* **14**, 34955 (2022).
21. S. Morales-Cámara, L. Cardona-Carrascosa, P. Salcedo-Abraira, A. Rodríguez-Diéguez, S. Rojas, *Cryst. Growth Des*. **25**, 4685 (2025).
22. S. Morales-Cámara, B. Parra-Torrejón, A. Rodríguez-Diéguez, J. M. Delgado-López, G. B. Ramírez-Rodríguez *et al.*, *ACS Appl. Mater. Interfaces* **16**, 29305 (2024).