Water treatment

https://doi.org/10.1038/s44221-023-00084-7

Extracting pharmaceuticals from water using metal–organic frameworks

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A metal–organic framework enables the removal of emerging organic contaminants from the effluent of a wastewater treatment plant.

Water pollution with anthropogenic contaminants is a potential threat to the environment and human health[1]. Of particular concern are emerging organic contaminants (EOCs) — compounds that were newly developed or discovered in the environment as well as recently categorized as contaminants. These include pharmaceuticals, personal care products, pesticides, veterinary products, industrial compounds, dyes and food additives[2].

A viable strategy to address this issue is the development of innovative technologies and materials capable of removing EOCs from water[3]. In this context, metal–organic and covalent organic frameworks (MOFs and COFs) — porous, crystalline compounds made from inorganic metal ions/clusters and organic linker molecules (MOFs) or exclusively from organic linkers (COFs) — are particularly promising due to their exceptional porosity and tunability, thus allowing for their design to be suitable for a variety of applications[4,5]. Indeed, these materials have been extensively investigated for the removal of EOCs from water through adsorption and/or catalytic degradation[6,7]. However, hitherto, only few studies focused on water sources containing a mixture of different contaminants at low concentrations, thus attempting to resemble real-world environmental conditions and demonstrating the practical utility of these materials to address the global problem of EOC presence in water.

Now, writing *in Nature Water*, Grape et al. show that a MOF, termed SU-102 — [Zr(ellagate)$_2$](dimethylammonium)$_2$; see Fig. 1a — can be utilized for the removal of EOCs from municipal wastewater treatment plant (WWTP) effluent[8]. Using this material, the authors were able to substantially reduce the concentrations of all 17 pharmaceutical EOCs identified at quantifiable concentrations after conventional treatment in a WWTP in Stockholm (Fig. 1b). Among others, these compounds included antibiotics, antidepressants, and anti-inflammatory drugs which are currently continuously released into the environment.

SU-102 was synthesized from a zirconium salt and ellagic acid (Fig. 1a) — a biomolecule that can be isolated from plant material and is considered a waste product of the food, pulp, and paper industries[9]. The strong metal–ligand interactions between the zirconium(IV) ions and the phenol-bearing organic ligands — a hard Lewis acid and base, respectively — endowed this framework with exceptional hydrolytic stability, thus making it ideally suited for long-term operation in aqueous solutions. Notably, the MOF is anionic and contains dimethylammonium counter-cations for charge-balancing in its pores after synthesis. These can be exchanged for alkali cations by soaking the material in a concentrated alkali chloride salt solution. Importantly, the authors demonstrated that the fully sodium-exchanged framework retains its ability to extract pharmaceutical contaminants from WWTP effluent, albeit with small losses to the EOC removal efficiency compared to the as-synthesized MOF.

As anticipated, the anionic framework SU-102 exhibited much higher removal efficiencies for positively charged EOCs in comparison to neutral and negatively charged species (Fig. 1b). This indicates that the development of novel cationic frameworks capable of efficiently capturing negatively charged EOCs would complement the adsorption capabilities of SU-102. Furthermore, the authors demonstrated successful regeneration of the adsorbent (removal of EOC molecules from the MOF) by soaking it in a concentrated sodium chloride solution, which was able to displace the guest molecules from the framework pores. This is an important capability which not only allows for reuse of the MOF material but also for potential recycling of the EOCs extracted from wastewater.

Another avenue for EOC removal from water is their catalytic conversion to less harmful components. This strategy might be a powerful method for continuous degradation of anthropogenic contaminants. In this regard, Grape et al. demonstrated that SU-102 is able to photocatalytically degrade the antibiotic sulfamethazine (out of three EOCs tested) under visible light irradiation (Fig. 1c). While these findings are encouraging, it leaves room for further material and method development to achieve catalytic degradation of a broad spectrum of EOCs. This will be particularly challenging because EOCs are usually present as a complex mixture in wastewater, leading to potential cross-reactivity between the EOCs and/or their degradation intermediates/products under exposure to the given catalytic conditions. Additionally, potential toxicity of the intermediates and the degradation products has to be taken into account, as has been done in the present study by tracking the decomposition with mass spectrometry and proposing degradation mechanisms.

It is clear that more efforts will need to be invested to design a comprehensive system for EOC removal from WWTP effluent. This could include the use of a mixture of different methods and materials, such as SU-102, each designed for highly efficient removal of a set of contaminants. Another possibility is the use of multivariate frameworks for adsorption or catalytic degradation, where the pore walls are lined by different functionalities[10] thus potentially allowing for tailoring a single material to exhibit high removal efficiencies for a diverse array of EOCs.

The study by Grape et al. made an important step towards demonstrating the capability of MOFs to effectively reduce the concentration of EOCs in real WWTP effluent. It is evident that a set of materials and/or methods might be necessary to remove all detectable EOCs in the wastewater by either adsorption or catalysis and the usage of MOFs could be part of this comprehensive system.

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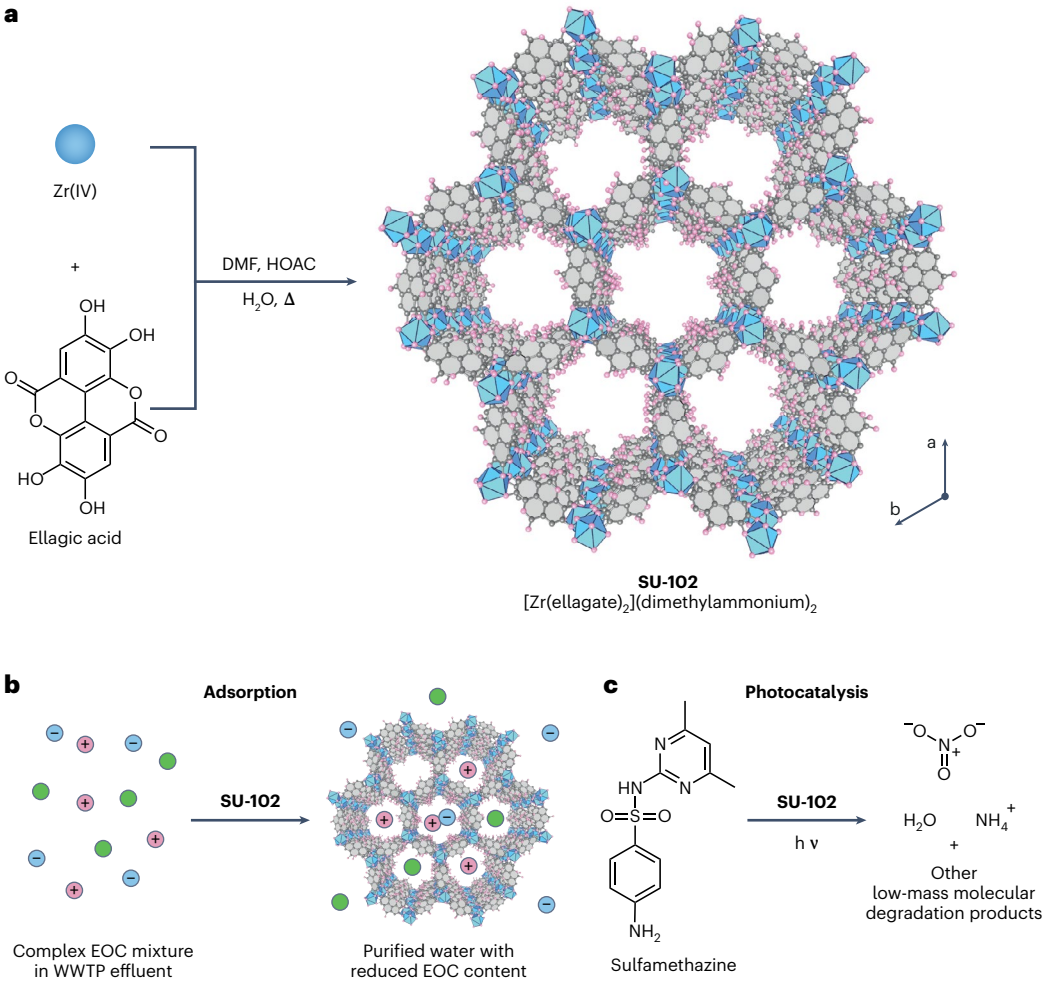

Fig. 1 | Synthesis, structure and pharmaceutical removal mechanisms of SU-102. a, Synthetic scheme and crystal structure of the MOF prepared under heating by utilizing a zirconium(IV) salt, ellagic acid, *N*,*N*-dimethylformamide (DMF), acetic acid (HOAc) and H_2O, resulting in the anionic framework [Zr(ellagate)$_2$]$^-$ with charge-balancing dimethylammonium counter-cations in its pores (not depicted). Blue (polyhedrons), zirconium; pink, oxygen; grey, carbon. Hydrogen atoms are omitted for clarity. Coordinate system is given for guidance. **b**, Removal of emerging organic contaminants (EOCs) in wastewater treatment plant (WWTP) effluent through adsorption. The EOCs and their charges at the pH of the effluent are represented by differently coloured circles with enclosed symbols (blue, singly negative; green, neutral; pink, singly positive). **c**, Photocatalytic degradation of sulfamethazine, an antibiotic drug, by visible light in presence of SU-102.

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Published online: 15 May 2023

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Competing interests

The authors declare no competing interests.