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Toxic Organophosphonate Captured And Degraded Using Macroscopic, Monolithic Metal-organic Framework Structures

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Metal-Organic Frameworks (MOFs) materials are researched for their high surface area and interaction capabilities with harmful chemical species. Zirconium-based MOFs can both adsorb and catalytically hydrolyze toxic organophosphonates, reducing risk of hazardous exposure. Many MOF crystal composites based on fibers, fabrics, and sponges are actively being explored to replace current activated carbon systems which can adsorb toxic chemicals but not degrade them. MOF composite systems often undergo heated syntheses, acidic conditions, and substrate incompatibility that can lead to unwanted characteristics such as poor MOF adhesion, low MOF loading, and/or a collapse in substrate structure.

This work focuses on the formation of macroscopic MOF structures with tunable dimensional and porous properties. Here we form UiO-66-NH2, an amine functionalized zirconium-based MOF, into macroscopic, monolithic structures without the reliance on any support material. Our method utilizes the formation of MOF sol-gel systems that allows for MOF crystals to connect into a porous network followed by solvent extraction to form MOF xerogel structures. Due to being a connected, macroscopic structure, concerns about poor MOF adhesion and MOF loading onto substrate surfaces are eliminated. This work has shown size tunability of the monoliths going from the millimeter to the centimeter scale as well as some control over the presences of a hierarchical porous nature exhibiting micro-, meso-, and macropores. UiO-66-NH2 monoliths formed have reached approximately two cm with specific surface areas of 900 m2/g, comparable to crystalline powder. Early testing shows that the xerogel structures outperformed compressed MOF powder pellets in hydrolyzing DMNP, an organophosphonate nerve agent simulant. The results in this work provide insights on creating macroscopic, monolithic MOF-only structures with tunable properties that can be further adapted to applications of catalysis and filtration.

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