The rise of industrialization over the past century has escalated water pollution and related problems globally. Unsafe drinking water not only jeopardizes human health, in most severe cases leading to death, but also causes serious environmental contamination, thus posing a dangerous ecological threat. Most toxic water-polluting agents mobilize in aquatic environments such as lakes, rivers, oceans, groundwater, etc., which makes it difficult to separate them by a common energy-efficient technology. In this issue of ACS Central Science, Ghosh and co-workers explore a novel functional hybrid porous material composed of a metal–organic polyhedra (MOP) and a covalent organic framework (COF), which, by the virtue of its unique design and adsorption ability, effectively and selectively captures toxic oxoanions from water. Their work presents a new avenue for water purification and amelioration.1

Porous materials such as metal–organic frameworks (MOFs), covalent organic frameworks (COFs), and MOP have been in the limelight in the past few decades because of their promising potential for applications in various areas related to energy and the environment. The molecular building block approach in designing these materials results in exciting hierarchical architectures with functionalities that could tackle key global problems. Environmental remediation by porous matrices that capture toxic entities has received tremendous attention over the past several years.2

The capture typically follows adsorption-based mechanisms, and systematic tunability of these porous materials has led to greatly enhanced selectivity, fast kinetics, and excellent reusability—all required for practical purposes.3 Of the various toxic elements, inorganic oxoanions are a major source of pollution in drinking water. For example, even trace levels of arsenic in the form of arsenite (As(III)) and arsenate (As(V)) in drinking water can cause severe cardiovascular and neurological disorders, skin cancers, stillbirth, etc.4 Therefore, capturing such toxic species in water is of paramount importance and contextual from the standpoint of human health and environmental preservation. In this work, the authors employ an intriguing strategy to covalently link an MOP and a COF to generate an anion
exchangeable hybrid material that exhibits exceptional performance for capture of metal- and metalloid-based oxoanions. The MOP used in this study is a Zr-based molecular species\(^5\) comprising a cationic trinuclear Zr cluster and free exchangeable chloride (Cl\(^-\)) ions. The nanosized cationic MOPs were grafted onto an iconic COF, i.e., TpPa-1,\(^6\) following a two-step procedure: (a) first treating the free amine groups of the organic struts of the MOP with 1,3,5-triformylphloroglucinol, and (b) reacting this aldehyde functionalized MOF with excess 1,3,5-triformylphloroglucinol and \(p\)-phenylenediamine. This produced a unique covalently linked MOP/COF hybrid material (Figure 1a) referred to as IPcomp-3(200) [IP stands for IISER-Pune, comp stands for composite, 200 is the amount (in mg) of MOP used in the synthesis]. The COF matrix acts as a rigid porous anchor facilitating the exposure of active sites of the MOP molecules to targeted oxoanions—an otherwise difficult target to achieve in solitary MOPs. IPcomp-3(200) was characterized thoroughly to confirm the presence of the individual components, i.e., the MOP and the COF.

Because of the cationic nature of the hybrid material, the authors performed the conventional anion exchange experiments with oxoanions, viz. HAsO\(_4^{2-}\), SeO\(_4^{2-}\), CrO\(_4^{2-}\), Cr\(_2O_7^{2-}\), MnO\(_4^-\), and ReO\(_4^-\) (a model anion for radioactive TcO\(_4^-\)) using IPcomp-3(200). The hybrid material achieved the remarkable feat of entrapping toxic oxoanions in the presence of 1000-fold excess of other competing anions, viz. Cl\(^-\), NO\(_3^-\), Br\(^-\), SO\(_4^{2-}\), ClO\(_4^-\), etc. Since industrial wastewater and groundwater contain a plethora of different anions, this hybrid material’s highly effective way of capturing of toxic oxyanions could pave the way for designing commercial materials for water purification.
The authors also observed that this capturing technique has superior kinetics and nearly 100% efficiency in removing toxic oxoanions (concentration = 1 ppm) within seconds (Figure 1b). As a prototype demonstration, the authors showed selective capture of As(V) by IPcom-3(200) in drinking water with excessive competing anions, thus achieving a significantly low concentration of As(V), ca. <10 ppb (Figure 1c). Similarly, Cr (VI) ions showed a decrease of concentration by >95% when passed through a column packed with IPcom-3(200). To demonstrate the practical utility of this material, Ghosh and co-workers collected groundwater samples from various parts of India and reduced the As(V) concentration from 40–50 to <10 ppb using the hybrid material filter. This value is well below the permissible limit, set by WHO, for As(V) concentration in drinking water.7

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The authors rightly called this material a “nanotrap grafted hybrid material” as the MOP acts as a nanotrap scavenger for toxic oxoanions by virtue of its active Zr cluster and exchangeable Cl− ions. The COF functions as a porous support anchoring the MOP nanotraps, thus allowing maximum exposure of the active sites. The covalent linkage between the MOP and COF offers additional stability and prevents leaching of solitary components from the hybrid composite after multiple uses.

Overall, this exemplary research by Ghosh and co-workers offers a new and promising approach for efficient environmental remediation by MOP/COF based hybrid materials. Its superior selectivity, fast kinetics, and low cost are critical for designing smart materials for water purification and wastewater treatment. Although the commercial viability of this hybrid material needs to be explored further, the work certainly sheds light on some unexplored territories of environmental research.

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