

Metal organic frameworks (mofs)



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In 1989, Robson introduced metal organic frameworks (MOFs) as a combination of transition metals and organic ligands cluster that are well-known for their highly porous structure, tunable architecture and high surface area. MOFs provide diverse applications in advanced chemistry such as catalysis, drug delivery, separation, magnetism and etc. There is no organized nomenclature system for MOFs. Abbreviations are associated to an institute, where they were initially characterized, incorporating with different numbers if different MOFs have been obtained within the institute.

O. M. Yaghi's group were pioneer in the code of MOFs. For example UiO corresponds to University of Oslo, and MIL to Matériaux de l'Institut Lavoisier. HKUST-1, generated at the Hong Kong University of Science and Technology; and MOF-5, introduced by Yaghi in 1999 that known as two unusual created varieties with an internal surface area of minimum 2, 300 square meters per gram enough to cover more than eight tennis courts. Nowadays, there are MOFs with internal surface areas three times more than MOF-5. High internal surface area of MOF leads to accept more guest molecules in its assessable cavities.

The major point of creation of the stable MOFs is the use of metal atom clusters as the nodes, rather than single ions. The geometry of these clusters determines the overall shape of the crystal, which can be joined together with plenty of organic linkers. The superiority of metal clusters-based nodes compared to their organic (carbons) or inorganic counterparts (zeolites, silica) is their cavity size and spatial hole arrangement which can be precisely designed. Zeolites provide building blocks of the metal ions with

different organic linkers to fabricate an infinite number of new MOFs with diverse architectures, topologies, and cavity.

Zeolitic imidazolate frameworks (ZIFs) are made up of different metal atoms such as (Co, Cu, Zn, etc.) linked through N atoms of imidazolate (Im) or functionalized Im ligands to make four, six, eight, and twelve member ring MN₄ tetrahedral clusters. ZIFs show similarity to zeolites framework structure in the T-O-T bridges (T = Si, Al, P), that are replaced by M-Im-M bridges (M = Zn, Co, Cu) with 145° bond angles for both. MOFs show diverse ingredients in their structure beside larger panel of cavity sizes and topologies (tunnels, cages, etc.) in comparison to zeolites. Flexible porous structure of MOFs leads them to be a good adsorbent in the sample matrix. Moreover, presence of different organic linkers like polycarboxylates, phosphonates, sulfonates, imidazoles, amines, pyridyl and phenolates lead to introduce an infinite number of MOFs.

This phenomenon provides ordered structures like scaffolding, with large pores and surface area for trapping compounds. Crystalline structure of MOFs provides organized pores and cavities in the equal diameter within framework. This well-organized structure is achieved by a reticular synthetic approach. Specific design of the coordination network is formed when the metal compartments are considered as secondary building units (SBUs) which can be linked to the network through convenient organic linkers. Therefore, MOFs are able to adopt specific pore size and surface morphology. Possesing the highest surface area, good thermal and mechanical stability, nanoscale and stable cavities in structure, regular pore topologies, ultra low densities, high adsorption affinity, tailorable to integrate

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functional moieties on the framework backbones, as well as modifiable pores and cavities are some of specific properties of the MOFs. Modification of the organic linker with grafting the polar or non-polar functionalities represents another advantage of MOFs with new physicochemical properties.

There are few commercial solid phase extraction (SPE) adsorbents which are developed for analysis, whereas it is of great importance to design new advanced compound as efficient adsorbents for SPE extraction methods. To date, various types of adsorbent materials have been investigated.

Mentioned superior properties of MOFs encourages the researches to apply MOFs as novel adsorbents in various SPE techniques. However, there are limitations for designing classic columns packed with MOFs due to their inappropriate particle size and morphology which needs to be engineered for application of MOFs as SPE materials. For this purpose, MOFs could be coupled with in flow-through devices like monolithic columns or polymer disks or directly used in D- μ -SPE adsorbents technique.

Solid phase microextraction (SPME)

Recent studies in SPE have been focused on miniaturization of the extraction techniques to enhance the extraction efficiency and overcome limitations raised from conventional methods. Solid-phase microextraction (SPME), which was introduced by Pawliszyn and his group in 1990 as a solvent-less sampling technique. SPME revealed a significant insight in the field of sample preparation to moderate the operation time and chemical consumption of the solvents in comparison with traditional SPE. Therefore, SPME gained tremendous popularity as a solvent-free procedure.

Micro solid phase extraction (μ -SPE); static mode

MOFs are among the significant material as μ -SPE fiber coatings. Polycyclic aromatic hydrocarbons (PAHs) are important organic pollutants with two or more fused benzene rings in their structures often found in the different environmental medias. An investigation revealed that the MOF-5 is a suitable μ -SPE adsorbent for the determination of PAHs with HPLC in environmental matrices. Moreover, MIL-101 was used as a μ -SPE adsorbent for efficient enrichment of five organochlorine pesticides followed by GC/MS. This study demonstrated a new application of MIL-101 using hollow fiber membrane bag to protect the adsorbent in complex aqueous matrices.

In another study, Salarian et al. demonstrated that a kind of MOF sustained by a nano-sized Ag₁₂ cuboctahedral node, could be applied to selective extract of traces amounts of lead (II) from environmental water samples using flame atomic absorption spectroscopy (FAAS). The use of MOF resulted in excellent enrichment and good adsorption of lead (II). One of the common drawbacks of μ -SPE is the fiber fragility which should be taken into consideration. Yan' group presented many studies on MOFs in the separation field. They introduced a thermal and solvent stable MOF MIL-88B with nanosize bipyramidal cages and large surface area. Synthesized MIL-88B was applied as fiber for developing μ -SPE method to determine polychlorinated biphenyls (PCBs) that is another type of persistent organic pollutants. This method provided 757–2243 enrichment factor. This excellent enrichment level was attributed to the hydrophobicity and dipole–dipole interactions between PCBs and MIL-88B. The diphenyl structured PCBs and the aromatic

framework of MIL-88B may lead to the strong hydrophobic interaction between the PCBs and the MIL-88B.

Yan' group also introduced another SPME fiber, coated with UiO-66 for extraction of phenols from water samples. Headspace SPME fiber was coated with UiO-66 and provided enhancement factors of 160 and 3769 for phenol and (2, 4-dichlorophenol), respectively. This good extraction performance was related to the hydrophobicity of the phenols, the hydrogen-bond interaction between the hydroxyl groups of the phenols and the ZrO sites. Besides, the π - π interaction between the phenols and the UiO-66 framework played an important role in the high extraction efficiency. Furthermore, a facile in situ solvothermal method was reported for immobilization of MOF-ionic liquid functionalized graphene composite (MOF-5/ILG), on etched stainless steel wire.

The proposed method was applied to determine two kinds of antibiotics in milk, honey, urine and serum samples with acceptable relative recoveries of 82.3–103.2%. ZIFs have received considerable attention as a novel porous material for open-tubular column in online in-tube method due to their fascinating structures and unique properties. In a study, ZIF-8 was used as a adsorbent for micro-solid-phase extraction of six PAHs from environmental water samples for the first time. A novel bio-inspired polydopamine (PDA) material was applied to immobilize ZIFs inside the chemical resistance poly(ether ether ketone) (PEEK) tube for online SPME of six PAHs.