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A critical review about metal organic framework-based composites: Potential applications and future perspective

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ABSTRACT

The properties of metal-organic frameworks (MOFs), a potential class of porous crystalline materials with a wide range of uses, depend on their structural details, including compositions and architectural designs. Through functionalization and their interaction with other nanomaterials, MOFs' structure and design have undergone changes as a result of their extensive research. Numerous outstanding evaluations on single MOFs, MOF-based composites created through conjugation with non-MOF materials, and their derivatives have summarized the developments in the field of MOFs. A thorough examination of MOFs and their combination is, however, lacking. In this perspective, we present a current and thorough description of the accomplishments of MOF-based hybrids below. First, a description of the synthetic strategy/formation process is provided to illustrate how host and visitor MOFs interact. The structural diversity in MOF-based systems is then thoroughly examined to show how MOF systems enable advancements in abased composites for a variety of applications, particularly in the medical and environmental fields. Finally, we present our personal opinions on the difficulties and potential paths for the development of MOFs materials.

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1. Introduction

Bivalent or trivalent aromatic carboxylic acids or N-containing aromatics are frequently utilized to build frameworks with gold, zinc, copper, chromium, aluminum, zirconium, and other elements in metal

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organic frameworks (MOFs), a family of crystalline organic-inorganic hybrid compounds [1-4]. The structure of the framework, inorganic metal centers, and organic ligands are the three primary components of MOF. If MOFs were created by expanding zeolite topology, their inorganic and organic structures would have larger pores and higher porosity than zeolites. The enlarged size of inorganic SBUs and the network's

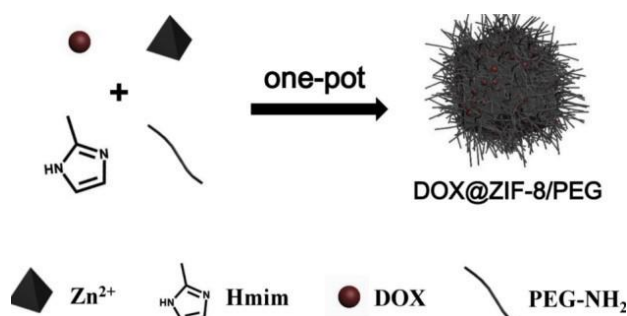


Fig. 1. One-pot synthesis of poly(ethylene glycol) modified zeolitic imidazolate framework-8 nanoparticles: Size control, surface modification and drug encapsulation. Reproduced from Elsevier [35].

dimensions caused by big metal clusters are the causes of the huge pore size. Additionally, a combination of high porosity and longer organic ligands that benefit big pore width account for the length of the link between inorganic SBU. When various metal centers and ligands are used to create MOFs as molecular building blocks, the resulting flexibility allows for the modification of both physical and chemical properties [5]. MOFs are synthesized through various procedures such as surface modified encapsulation, in situ generation in MOF's cavities, self-sacrificed template method, microwave assisted methods, room temperature based procedures, step-by-step construction of the sandwich-like heterostructure, and one pot synthetic method [2,3,6,7]. Due to MOFs' exceptional qualities, these materials are now widely used in a variety of fields, including medication delivery, sensing, and gas storage [8,9]. The syntheses of MOF-based composites or their use in the catalysis or sensing domains were the focus of many outstanding publications that discussed the synergistic effect between MOFs. In contrast, it is currently unclear how the functions of MOF component parts relate to their actual applications. In fact, according to some studies, MOFs' distinct internal structures and properties—rather than those of other integrated functional materials—are the primary cause of the improved performances and expansion of MOF-based composite functionalities. Therefore, it is crucial to clarify the function of MOFs in composites in order to comprehend how the structure and functionality of materials based on MOFs relate to one another.

This paper summarizes current developments in MOF-based composites in an effort to better understand the structure-performance relationship of MOF-based composites, with a focus on the practical uses of MOF components. First, common techniques for producing MOF-based composites are discussed, along with benefits and drawbacks. Next, according to the functions of MOF components in MOF-based composite applications, the impact of internal composition, structures, and properties of MOFs as well as external encapsulation status characteristics on the performance of composites is discussed, with a focus on their use in the medical field and environmental remediation. Then, contemporary problems with these composites are given and discussed. To further pique the curiosity of chemical aficionados, we think that the review will give readers a better grasp of MOF-based composites for more carefully managed manufacturing and application.

2. MOF-based composites

The crystalline porous materials known as Metal-Organic Frame-

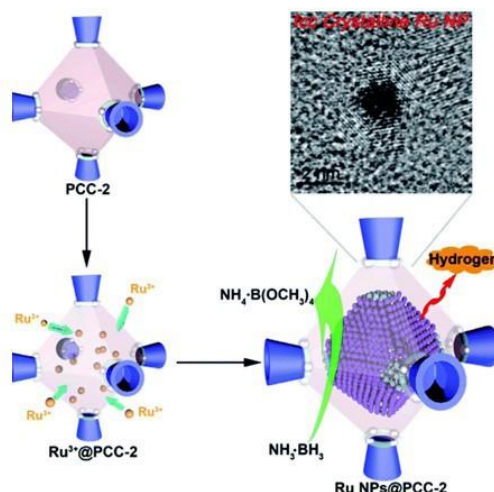


Fig. 2. Scheme representing the synthesis of fcc Ru NPs via PCC-2 as the template. Reproduced with permission from Elsevier [37].

works (MOFs) are created when core metal ions or clusters self-assemble with bidentate or multidentate organic ligands using coordination bonds [1,10]. Since their discovery in the early 1990s, MOFs have been the subject of intense research because of their highly organized porosity, extraordinarily high internal surface areas, and adaptable architectures. As a result, MOFs swiftly gained popularity as materials for almost two decades [11]. Up to this point, significant efforts have been made to create MOFs with novel structures and properties and to explore their potential uses in a variety of industries, including gas adsorption/separation, catalysis, sensors, drug delivery, magnetic materials, and optical devices [12–14]. Unfortunately, there are several instances where the performance of MOF materials is less than ideal, and there is still much work to be done to increase their applicability [15].

MOFs have advantages over conventional porous materials in terms of shape and characteristics, allowing open channels to be constructed and carefully tuned utilizing various metal nodes and organic ligands in accordance with intended uses [16]. MOFs are excellent host platforms for the immobilization or encapsulation of various functional materials, such as nanoparticles (NPs), quantum dots, polyoxometalates, enzymes, and polymers, because of their structural diversity and adaptability [17–19]. As a result of the materials' synergy, MOF composites always display significantly improved or even unique features when compared to single-component materials [20].

Technically, the constrained environment produced by the MOF cavities might significantly increase the catalytic activity of embedded NP catalysts [21]. MOF composites may be used to create sensors that can identify the size of molecules by utilizing the barrier effect in MOF channels on the flow of foreign molecules [22]. Additionally, it was discovered that after being enclosed in MOFs, fragile enzymes may display great tolerance under challenging circumstances while maintaining high activity [6,15,23]. In order to further improve their performances and broaden their applications, MOF-based composites have drawn growing research attention. As a result, significant effort has gone into designing and building different MOF-based composites. However, despite the great progress, achieving functionality between the MOF host and guest species is still challenging for specific applications of MOF-based composites. Hence, it is vital to identify the structural–functional relationship in MOF composites to efficiently and directionally synthesize specific MOF composites for particular applications.

The synergistic relationship between MOFs and other functional materials has already been covered in a number of outstanding reviews [26,27]. The majority of them concentrated on the creation of MOF-based composites or on using them in catalysis or sensing sectors [28]. In contrast, it is currently unclear how the functions of MOF component

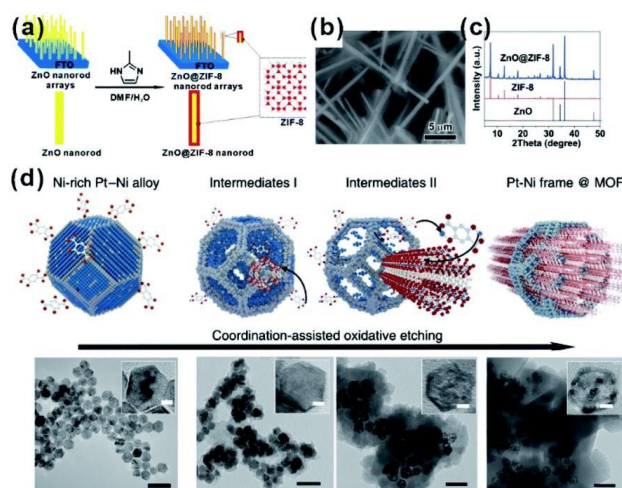


Fig. 3. Schematic of ZnO@ZIF-8 nanorods made using the self-template method is shown in Fig. 3(a). (b) A SEM image of ZnO@ZIF-8 nanorods, and (c) an XRD pattern. Reproduced with permission from ACS [39].

parts relate to their actual applications. In fact, some research revealed that instead of the properties of other integrated functional materials, the better performances and expansion of MOF-based composite functions mostly originate from the unique internal structures and properties of MOFs [29]. In order to better comprehend the relationship between the structure and function of MOF-based materials, it is crucial to clarify the role of MOFs in composites.

Many different combinations of nanomaterials and MOFs can be used to create MOFs-based composites, which enable the achievement of a wide range of functions and characteristics. Composites made from MOFs are appealing for a variety of applications due to their many benefits. Several of these benefits include:

High surface area: Composites based on MOFs have high surface areas, making them suitable for catalytic and adsorption processes.

Porosity: Composites based on MOFs are porous, which makes them good for storing and separating gases.

Tunable characteristics: A wide range of functionalities and properties can be attained by synthesizing MOFs-based composites from a variety of metal ions and organic ligands.

Chemical stability: Composites based on MOFs may exhibit strong chemical stability, making them appropriate for usage in challenging conditions.

Synthesis simplicity: Scalable production is made possible by the simple and moderate synthetic conditions that may be used to easily produce MOFs-based composites.

Crystalline structure: MOFs-based composites may be characterized by X-ray diffraction and designed with the aid of computational models thanks to their clearly defined crystalline structure.

3. Synthesis

The properties and the performances of MOF-based composites are directly related to the MOFs structure, design and structure. For the synthesis of MOF-based composites, there five roots could be used; (i) surface modified encapsulation, (ii) in situ generation in MOF's cavities, (iii) self-sacrificed template method, (iv) step-by-step construction of the sandwich-like heterostructure, and (v) one pot synthetic method.

3.1. Surface modified encapsulation

This technique also called “build-bottle-aroundship” and it is based on two major steps: (i) preparation of well performed NPs with unique and uniform size, design, structure and morphology and then (ii) the

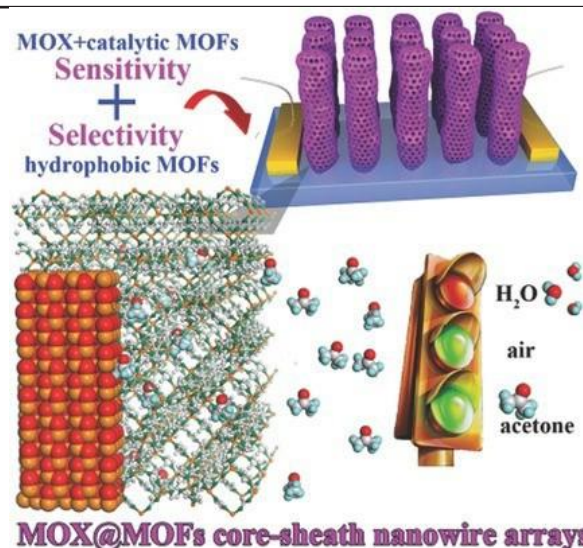


Fig. 4. For the first time, a method for creating novel materials for sensing volatile organic molecules is proposed, combining metal oxides and metal-organic frameworks.

MOF will be grown on the surface of the prepared NPs creating great lattice structure barriers between MOFs and encapsulated materials, leading to self-nucleation of MOFs instead of forming the encapsulation structure. To overcome such barriers, structure-flexible materials have been used bridges to connect MOFs with encapsulated materials.

For instance, to correct the lattice mismatch at NP@MOF surfaces, several authors treated NPs with surfactants PVP and CTAB afterwards [30]. In addition to surfactants, metal oxides or hydroxides may be used to alter NPs and build MOFs [31,32]. NPs of different shapes and sizes can be enclosed inside MOF shells using encapsulation. Other materials, including carbon-based compounds, polymers, and even enzymes, might be employed in place of these nanoparticles to modify the MOFs surfaces using this technique [33,34].

Unfortunately, this technique could be time-consuming which require more effort to find new ways and alternative to improve this technique. In this context, a study reported a simple and rapid synthetic method that combines the size control of ZIF-8 NPs and their surface modification of PEG at the same time. Monovalent amino PEG (PEG-NH₂) was used as capping agent to control the size of ZIF-8 and simultaneously realize surface modification through coordination interaction. The size of ZIF-8 was tuned in a broad range. The coated NPs showed intact crystalline structure with improved colloidal stability. By further adding the anti-cancer drug doxorubicin (DOX) into the reaction mixture, ZIF-8 NPs with encapsulated DOX and PEG surface modification (DOX@ZIF-8/PEG) can be synthesized in one-pot (figure 1) [35].

3.2. In situ generation in MOF cavities

This method involves first diffusing precursors of the embedded material into the MOF cavities, then in situ transforming the target materials there. Here, the difficult issue is the production of the materials utilized for modifications in the cavities of the MOFs rather than on their surfaces, which may restrict the applications of this technology and also restrict the performance of the created MOF-based composites [36].

Nevertheless, there are still some issues with in situ generation. First off, the interior structures of MOF templates may be somewhat damaged during the process of forming embedded materials. Additionally, it is difficult to comprehend the structure-performance relationship of MOF-based composites since it is difficult to manage the morphology, surface structure, and density of embedded elements.

The in situ generation method has produced NPs with pristine surface topographies without modification with organic surfactants like CTAB and PVP. Additionally, NPs constrained by MOF cavities seemed

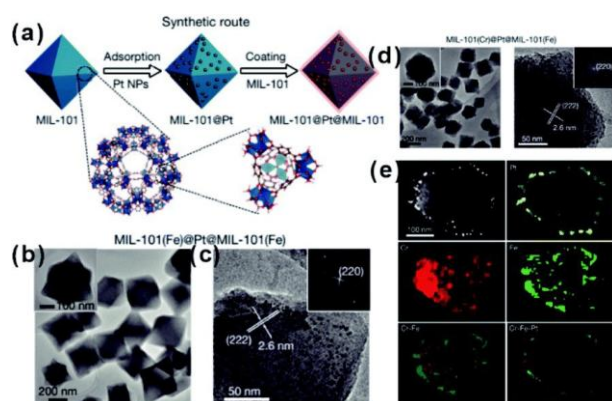


Fig. 5. Synthetic process of sandwiched MIL-101@Pt@MIL-101 composites is shown in Fig. 5(a). (b and c) TEM pictures of the MIL-101(Fe)@Pt@MIL-101 in their prepared state (Fe). (d) TEM images of the MIL-101(Cr)@Pt@MIL-101(Fe) as prepared; (e) associated HAADF-STEM image; and (f) elemental mapping images. Reproduced with permission from nature [48].

relatively tiny and consistent in size, advantageous for real-world uses. Surprisingly, under benign conditions, an in situ reaction in MOF cavities serving as nanoreactors can easily produce NPs with certain unique shapes and compositions. For instance, using a truncated octahedral inner cavity (diameter 2.5 nm) of a porous coordination cage (PCC-2) as the nanoreactor, Zhou et al. created uniform truncated octahedral face-centered-cubic (fcc) ruthenium (Ru) NPs with exposed 111 and 100 planes, which is frequently challenging [37].

3.3. Self-sacrificed template method

Controlling the encapsulation status of embedded elements within the MOF matrix alone is crucial for MOF-based composites since it has a substantial impact on the practical performances, particularly in catalysis and sensing. Although many different approaches to building well-defined NP@MOF composites have been tried, it can be difficult to identify generalized paths. The self-sacrificed template technique works well for creating hollow or core-shell nanostructures because of the characteristics of solid reaction and relatively slow kinetics [7,38].

(d) A diagram of the coordination-assisted oxidative etching procedure and the related TEM images (scale bars represent 50 nm). Magnified TEM pictures are insets (scale bars represent 5 nm). Reproduction permitted. Nature Publishing Group [40].

Finding the right template materials and reaction conditions is essential for the successful fabrication of NPs@MOF composites using a self-sacrificed template. The release rate of metal ions from the template must match the coordination rate with organic linkers in order to ensure the formation of the MOF shell on the self-sacrificed template surface rather than in solution. Our team was the first to create metal oxide semiconductor@MOF composites using the self-sacrificed template method; ZnO nanorods served as both a template and a source of Zn for the creation of ZIF shells [39]. Both metal oxides and alloys containing transition metals can be used as template materials in the self-sacrificed template approach, which is straightforward and applicable to all materials [39,41]. For instance, Wu and Li et al. effectively created PtNi@MOF-74 composites using a coordination-assisted oxidative etching technique by using PtNi alloy NPs as a template [40].

The self-sacrificed template route has some limitations when it comes to template selection when compared to other approaches, but it provides a possible route to finely control the structure, thickness, and morphology of MOF shells. For example, the research team successfully

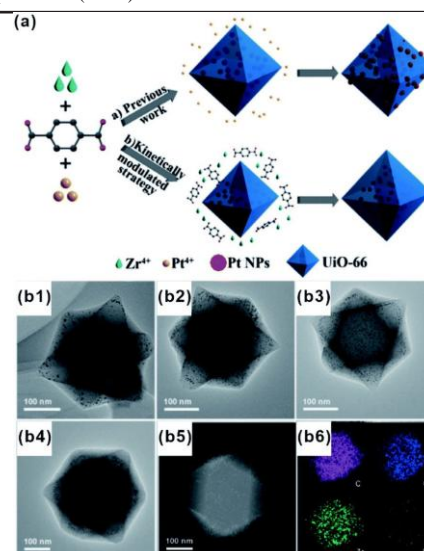


Fig. 6. MOF properties and their applications in gas storage and separation.

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controlled the thickness of the MOF shell in the nanoflower-like RhNi@MOF-74(Ni) synthesis by tuning the Ni content in the self-sacrificed RhNi alloy template [41]. Additionally, we employed 2,5-dihydroxyterephthalic acid or 2-methylimidazole as etching agents to selectively dissolve Ni or Co components of RhCoNi ternary alloy NCs to create MOF-74(Ni) and ZIF-67(Co) shells, respectively, on the alloy surface [42]. The as-prepared composites appeared promise as adaptable platforms to comprehensively explore the relationship between performance of composites and structure of MOF shells due to the significant disparities between the two obtained MOF shells in terms of aperture/cavity size. Another metal source can be added while MOFs are still being formed to create multicomponent MOF shells [43].

The self-sacrificed template method was used to create several MOF-based devices in sensor and catalysis applications in addition to creating MOF-based composite nanoparticles [44]. By depositing a layer of ZIF-CoZn thin film on a ZnO nanowire array using a self-sacrificed template approach, for instance, the ZnO@ZIF-CoZn gas sensor was created. Foreign Co²⁺ was also engaged in the synthesis of ZnO@ZIF-CoZn, in addition to the dissolved Zn²⁺ from the ZnO nanorod, which resulted in the development of the dual metal MOF thin film on the ZnO nanowire array [45].

The constructed ZnO@ZIF-CoZn core-sheath nanowire arrays exhibit significantly improved performance in terms of selectivity, responsiveness, recovery behavior, and working temperature. Reproduced with permission from Wiley [45].

As a result, the self-sacrificed template method's outstanding controllability gives more room to construct various structured MOFs on the NP catalyst surface, permitting detailed investigation of the structural-functional relationship in MOF-based composites.

3.4. Step-by-step construction of the sandwich-like heterostructure

As was already indicated, it can be difficult to limit the creation of functional materials inside or outside MOF matrices. Not only does the random distribution of functional NPs in the MOF matrix result in poor practical repeatability of MOF-based composites, but it also has a significant impact on the investigation of the true structure-function connection. Tang et al. created sandwich-like MOF-supported metal catalysts to address this issue by growing additional MOF layers on top of the catalysts [46,47].

They first created MIL-101 that was loaded with Pt NPs, and then, around the already-made Pt@MIL-101 particles, they epitaxially developed a new MIL-101 shell with a variable thickness [48]. Due to the fact that all Pt NPs were encapsulated in the incredibly thin MIL-101

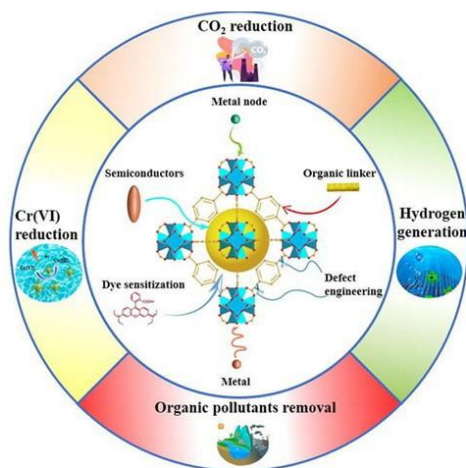


Fig. 7. Modified UiO-66 as photocatalysts for boosting the carbon-neutral energy cycle and solving environmental remediation issues. Reproduced with permission from Science direct [100].

layer, substance diffusion was unaffected (Fig. 6). When hydrogenating the C–O functional groups of α,β -unsaturated aldehydes, the resultant MIL-101@Pt@MIL-101 sandwich-like catalysts displayed remarkable selectivity. Be aware that the total catalytic efficiency of sandwich-like heterostructures depends critically on the thickness of the outer MOF shell. Thick shells will impede reactant and product diffusions, significantly lowering the reaction conversion even though selectivity should be increased to the same degree [47].

3.5. One-pot synthetic method

Each of the strategies discussed above requires a number of steps. In fact, a few instances showed how MOF-based composites might be made in a single step. For instance, Liu, Tang, and colleagues directly combined MOF-5 and Au precursors to create Au@MOF-5 [49]. The core-shell structures were produced by one-pot synthesis, where the Au precursor was first converted to Au NPs by dimethyl formamide (DMF), and then MOF-5 spontaneously developed newly generated Au NP surfaces. One-pot synthesis depends on controlling the development rate of MOFs and/or the rate at which metal ions reduce. As a result, Luque and Li et al. were successful in controlling the encapsulation of “clean” Pt clusters within UiO-66 by using a unique, kinetically controlled, one-step technique [50,51]. The use of a DMF solvent was crucial to the method’s success. In order to create Pt@UiO-66 composites, DMF and its minor byproduct of oxidation (Me₂NCOOH) would serve as a “bridge” to join MOF precursors to as-reduced Pt clusters, causing MOFs to develop anisotropically around the Pt surface. Although relatively straightforward and effective, one-pot synthesis is sadly not a widely used tactic. A group of substances known as metal-organic frameworks (MOFs) are composed of metal ions or clusters joined by organic ligands. They are highly porous materials with tunable properties that are appealing for a variety of applications, including gas storage, separation, and catalysis. Figure 6. Pt NPs are incorporated into MOFs using an in situ one-step technique and an in situ one-step strategy with kinetic modulation (Fig. 7(a)). (b1–b4) TEM pictures of Pt@UiO-66 nanocomposites made using various H₂/air volume ratios. A (b5 and b6) HAADF-STEM picture of Pt@UiO-66 with the associated elemental mapping. Reproduced with permission from Wiley [51].

4. Applications

Metal-organic frameworks (MOFs) are a relatively new class of materials with a wide range of possible uses. As a result, research on them is

now being conducted in both academic and professional settings. These possible uses comprise:

4.1. Gas storage and separation

Gas separation and storage are strongly tied to many facets of human life, including energy use, industrial output, and environmental protection. In particular, the separation of carbon dioxide is essential for reducing the greenhouse effect, the storage of hydrogen and methane is necessary for the widespread use of clean energy, and the separation and storage of toxic gases like carbon monoxide and ammonia are crucial for pollution control and the synthesis of industrial chemicals. An emerging family of crystalline porous materials called metal-organic frameworks (MOFs) are made of inorganic metal nodes and organic linkers, and recently they have received a plenty of applications in this field [52,53]. The distinctive structural qualities of MOFs, such as high porosity, large surface area, tunable structure, and modifiable functionality, make them particularly promising to be employed in gas storage and separation when compared to other porous materials [54,55].

In this context, researchers should concentrate more on highlighting the desired chemical properties of MOFs for required performance for precise and effective separation of the aforementioned energy-related gases, including CO₂, H₂, and CH₄, and any additional harmful gases, such as CO and NH₃. Through careful regulation of pore size, great progress has been made in the hydrocarbon separation of acetylene/ethylene and propylene/propane [56,57].

Additionally, using logically constructed MOFs, effective acetylene storage at ambient conditions was also accomplished [58]. MOFs outperform the majority of commonly used porous materials like zeolite and carbons in terms of specific surface area, which ranges from 1000 to 10,000 m²/g. MOFs, which have such a vast surface area, are thought to have tremendous potential for storing gases like H₂ and CH₄. The key benefits of employing MOFs over conventional porous materials are their consistent pore size and controllability of the entire structure. By fine-tuning the size of the ligand, changing the functional groups on the ligand or metal sites, exchanging metal ions, or employing the cooperative regulation of ligands and metal sites, isorecticular chemistry within MOFs makes it simple to obtain high H₂, CO₂, CH₄, and C₂H₂ storage [59,60]. Recently, a number of start-up companies that make MOFs have flourished, advancing the field of employing MOFs for adsorption to a new level. In light of this, this review article tries to summarize current advances in the use of MOFs for adsorption, both in the gaseous and liquid phases, while also incorporating the foundational knowledge needed to comprehend the adsorptive capabilities of MOFs. Adsorption applications with a list of the most promising structures and adsorption mechanisms are given priority. At the conclusion of the article, a personal perspective on the field’s future developments is offered. Although by no means comprehensive, this review tries to give readers a quick overview of the most recent developments in this field of study.

4.2. Catalysis

In recent years, there has been a noticeable increase in interest in catalytic chemistry [62]. Metal organic frameworks (MOFs), a family of porous materials, have generated a lot of interest recently due to their potential for use in catalysis [63–65].

It is well recognized that the cyclization of propargylic alcohols with CO₂ is a significant industrial reaction, and noble-metal catalysts are frequently used to achieve high product yields while maintaining environmental sustainability. For this reaction, a porous, noble-metal-free framework 1 with sizable, 1.66 nm-diameter 1D channels was created. Compound 1 has high acid/base stability and can even last one month in corrosive triethylamine. Furthermore, the biological macromolecule ethisterone was an uncommon substrate for this MOF catalyst to exhibit

catalytic activity [66].

In a separate study, compounds derived from manganese sulfide (MnS) were synthesized and used for the first time to activate PMS to break down the antibiotic levofloxacin (LVF) in water. In line with expectations, MnS significantly outperformed Mn_2O_3 in terms of LVF degradation efficiency via PMS activation. The findings of quenching studies, electro spin resonance identification, and electrochemical testing showed that the primary mechanism in the -MnS/PMS system was electron transfer progress. Additionally, it was determined how different environmental factors affected LVF removal and the capacity of -MnS to be reused, demonstrating the high application potential of the -MnS/PMS system. This study advances the fundamental understanding of -MnS-mediated PMS activation and offers helpful details for the actual use of manganese sulfide in water treatment [67].

Similar to this, another study revealed that copper- and calcium-based metal organic frameworks (MOFs) were successfully prepared and used as catalysts in the esterification and transesterification reactions for the manufacture of biodiesel from used cooking oil (WCO). The cubical structure of MOFs with a crystallite size of 50 nm and thermal stability below 600 °C is indicated by catalyst characterization. The catalyst has undergone testing for conversion of WCO to biodiesel, and the biodiesel samples meet ASTM requirements. The catalyst loading (X1), reaction temperature (X2), and alcohol-oil ratio (X3) are further process parameters that are improved using response surface methodology (RSM) via central composite design (CCD). To examine the dynamic interaction between process factors and biodiesel yield (YBD%), the second-order regression model is used. With the catalyst loading set at 1.0 g/100 mL, the reaction temperature at 60 °C, the alcohol-to-oil ratio at 20, and the biodiesel production at 84.5 (vol%), the ideal process parameters have been identified. The proportion of difference between experimental and projected outcomes is less than 5%, indicating good agreement. For three cycles, the regenerated catalyst significantly reduces the biodiesel production by up to 7% [68].

By adding sulfamic acid to the zeolitic imidazolate framework (ZIF-90), an effective bifunctional catalyst with synergetic Lewis and Brnsted acid sites was created in order to increase the acidic sites in catalysts to increase the conversion efficiency of microalgal lipids into biodiesel (SA). It increased the amount of Brnsted and Lewis acid sites when the sulfamic acid that joined with ZIF-90 through the imine bond (C N) delivered protons and disrupted coordinated Zn-N bonds in ZIF-90. The ratio of Brnsted acid to Lewis acid increased from 0.32 to 0.49, while the overall acidity of the ideal catalyst increased from 0.478 to 0.848 mmol/g. While Brnsted acid sites in bifunctional catalysts were more active in esterification reactions of free fatty acids, Lewis acid sites were more active in transesterification reactions of triglycerides in microalgal lipids. The result was that the best catalyst increased the conversion efficiency of microalgal lipids into biodiesel from 80.6% to 98.3% at 200 °C, while conversion efficiency remained 91.7% after 6 reusability cycles. The weight ratio of SA to ZIF-90 was 0.05 [69].

A calcium-terephthalate metal-organic framework ($[\text{Ca}(\text{BDC})(\text{H}_2\text{O})_3]$) was synthesized in a study using recovered terephthalic acid from waste polyethylene terephthalate (PET) as a precursor. Its ability to adsorb dye Alizarin red S (ARS) from an aqueous solution was examined for the first time. We looked into effective variables including pH, adsorbent dose (m), and starting ARS concentration (C). A proper relationship between the effective variables and either the removal percent (R%) or adsorption capacity (q) response was produced by BBD with 15 runs. For the following ideal conditions: pH = 6, m = 2 mg, and C = 379 mg/L, the suggested BBD model produced a maximum removal percentage (R% = 69.97) and adsorption capacity (q = 788.3 mg/g) of ARS. A Taguchi design with nine runs produced the best results at pH = 5, m = 2, and C = 300 mg/L. The Langmuir-Freundlich isotherm model well captures the adsorbent-adsorbate behavior since it has the

highest nonlinear R2 value (R2 = 0.9966) among the other isotherms. The highest amount of ARS that can be absorbed (qmax) is 979.0 mg/g. The experimental results are consistent with the PSO kinetic model (R2 = 0.9702) [69]. In a separate study, Co- and Ni-MFU-4l, a family of highly selective MOF catalysts for olefin upgrading, were the subject of in-depth X-ray absorption spectroscopy analyses that revealed the mechanisms underlying their deactivation. We further demonstrate that Ni-CFA-1, a more practical and cost-effective substitute for Ni-MFU-4l, replicates both the latter's excellent selectivity and local coordination structure in the ethylene dimerization catalysis. Unmatched in activity, selectivity, and cost among heterogeneous ethylene dimerization catalysts, Ni-CFA-1 activated by MMAO-12 reaches a turnover frequency of 37100 per hour and a selectivity of 87.1% for 1-butene under ideal circumstances. In a one-liter semibatch reactor, Ni-CFA-1 maintains its high activity for at least 12 hours, providing a path toward reliable and scaleable MOFs for industrial catalysis [70].

Metal organic frameworks (MOFs) are unique design platforms for biomimetic catalysts due to their varied chemical and physical properties, but they have had only patchy success thus far due to the instability of the MOFs used in physiological conditions. In this regard, the catalytic production of the bioactive compound nitric oxide (NO) from endogenous sources, S-nitrosothiols, is demonstrated using Cu(II)1,3,5-Benzene-tris-triazole (CuBTTri) (RSNOs). The CuBTTri-poly material retains its catalytic function for the production of NO once it has been prepared, with tunable release kinetics proportional to the total amount of CuBTTri embedded into the polymeric material and a surface flux corresponding to the therapeutic range of 1-100 nm cm2 min⁻¹. This function is maintained even after exposure to blood [71].

4.3. Sensing

The majority of modern sensing techniques rely on chromatography, including gas chromatography-mass spectrometry, liquid chromatography-tandem mass spectrometry, and high-performance liquid chromatography, as well as fluorometry, colorimetry, enzyme biosensors, and electrochemical methods [72-78]. These evaluation methods have a number of drawbacks, including time-consuming sample processing, expensive equipment, toxic chemicals, and expensive time-cost. Therefore, there is an urgent need for the expansion of an efficient method for determining various analytes that is accurate, easy, and time-saving [78,79]. Due to Metal-organic frameworks (MOFs) substantial thermal stability, high porosity, and huge surface areas, they have been used as detecting platforms for special analytes such as anions, cations, gases, organic small molecules, explosives, temperature, humidity, and pH, based on the eximious sorption kinetics, reversibility, and guest-induced changes in their structure and/or characteristics [80]. These features make MOFs a promising candidate for sensitive and selective sensors in environmental and industrial applications.

The focus is on optical MOFs because of their aromatic sub-units. Since aromatic linkers emit light [81], many MOFs have been discovered to be photoluminescent. The other type of MOF sensors are based on the powerful photoluminescence characteristics of lanthanide ions (Ln3+), which undergo luminescence variations [82] [83]. Due to the numerous 4f-4f transitions of the lanthanide centers and the clearly defined porosity of the frameworks, lanthanide MOFs, for instance, are discovered to be the ideal option for creating new fluorescence sensors [84]. Ln-doped MOF composites offer a novel class of fluorescence sensor for this purpose, which can detect gases, cations, anions, organic small molecules, humidity, temperature, and pH [85].

By modifying the electrode surface with various hybrid materials (such as functionalized graphene, preanodized/mediator-modified carbon substrates, and Au-based nanomaterials), it is possible to design new electrochemical sensors or biosensors with desirable analytical and

electrochemical features to use for standard environmental sensing or biosensing systems [86]. Selecting appropriate materials to combine with the frameworks may be able to overcome the MOFs' large empty volume limitation on conductivity [28].

In order to overcome this obstacle and serve as effective electrochemical sensors for environmental and biological targets, various MOF composite-based platforms have been created [87]. On the other hand, due to their exceptional physicochemical features, noble-metal nanoparticles (NPs) (such as Au, Ag, Pd, and Pt) can be anticipated in sensing, imaging, cancer therapy, optical data storage, and catalysis. However, because of their high surface energy, aggregation limits the aforementioned performances. In order to overcome this difficulty using numerous strategies, the researcher mixes them with MOFs. The resulting composites may be an excellent sensor for different chemical recognition [88,89].

In conclusion, MOF nanocomposites have been exploited for temperature sensing as well as the detection of a number of significant analytes, including heavy metal ions, anions, aromatic hydrocarbons, and hazardous phenolic chemicals. We believe that the knowledge presented in this review about the creation and use of MOF nanocomposites as photoelectrochemical sensors will aid the research teams in developing and establishing more sophisticated MOF-based sensing strategies. However, additional work needs to be done to enhance the MOF nanocomposites' sensing capabilities, particularly with regard to size, shape, design, and the functionalization of MOFs with many molecules by post-synthesis/dopant alterations and entrapment. Functionalized MOFs may also aid in the development of sensitive and selective sensors.

4.4. Water treatment and purification

Numerous methods for the preparation of MOF-based membranes have been developed since the introduction of MOFs to membranes in a variety of industries to improve their overall performance [90,91].

These methods have been applied to enhance the design of MOF-based membranes for liquid separation, especially in the desalination sector employing capacitive deionization [92], adsorption desalination [93], and membrane distillation [94], among others. Accurate and quick water purification depends on the proper design of MOF-based membrane manufacturing techniques. The development of preparation procedures, which have a substantial impact on the configuration of MOF-based membranes and their strength and removal effectiveness, is a significant determinant of the performance of MOF-based FO, RO, NF, and UF membranes in water treatment [92,95].

Although the fundamentals were established in the 1960s, the FO method has lately gained popularity for a variety of applications, most notably saltwater desalination [96]. For application in the water sector, scientists and engineers have looked for innovative methods for creating FO membranes. Although several porous matrix membranes (PMMs) have been employed for NF and UF membranes [91], FO-TFN membranes are less frequently used because of their structural resemblance to porous asymmetric membranes.

For FO applications, it is required to develop a very stable, active, and dense layer on the membrane's top surface in order to get over this restriction. By modifying the conventional dense film-casting method, Arjmandi et al. created a thin-film PMM mixed with magnetic water-unstable MOFs ((magnetic) ZnO@MOF-5) that significantly improved the performance of the FO process [97]. In a different work, a TFN membrane with a suitable 2D MOF (copper 1,4-benzenedicarboxylate) nano-filter in a polyamide active layer was created to improve water flux and anti-fouling capability without reducing selectivity for FO applications [98]. Controlling the internal concentration polarization is essential for enhancing FO performance. In order to improve the mass transfer efficiency in FO support substrates, Lee et al. used MOFs as a detachable

filler to create MOF-based PMMs [99]. They did this by managing the internal concentration polarization (i.e., using lower structural parameter values).

The degree of internal concentration polarization is frequently assessed using the structural parameter. Phase-in-version was used to create porous matrix substrates with three distinct types of MOFs by combining MOF particles with a polyacrylonitrile doping solution. The growth of comparatively large macropores inside the PMMs, which increased the mass (water/solute) transfer effectiveness inside the PMM substrate, was the cause of the improved FO performance. Liu et al. created self-standing dense and homogenous UiO-66 nanocomposite thin films (about 400 nm) integrated into polysulfone containing sulfonic functional groups using a straightforward solution casting process and solvent evaporation [100].

It has been widely documented that post-synthesis swapping or strengthening of UiO-66 in various noncovalent bonding forms enhances interfacial interaction with polymers [101,102]. In particular, during the thin-film deposition process, interfacial binding between UiO-66 and the sulfonated polysulfone might develop in thin films in situ. Because of its enhanced compatibility, the UiO-66, a zirconium-based MOF has a conformational reduced flexibility and backbones, increasing the mechanical and structural qualities of thin films strength [92].

4.5. Pharmaceuticals and Biotechnology

It is crucial to take into account a material's function and biocompatibility when using it in biomedical applications, especially those that take place in vivo. Some of the current MOFs might worry about the potential leaching of harmful metal ions or other components in their structure [103,104]. However, a couple of intriguing porous crystals MOFs were used as nontoxic medication delivery systems [105].

They must be built from components that are physiologically and ecologically acceptable for a variety of purposes. For instance, harmless MOFs were obviously preferred over hazardous ones in the majority of biological applications, such as drug delivery systems or intracellular imaging. Recently, researchers looked into the antibacterial activity of MOFs based on nontoxic antimicrobial cations [106,107]. Zinc-based MOFs are being introduced into bioapplication domains, especially as drug carriers, due to the low toxicity of zinc ions. Combining several antibiotic medications and materials allowed researchers to quantify the antibacterial activity [106]. In reality, dermatologists frequently utilized zinc, an endogenous low-toxic transition metal, as a cicatrizing agent, a skin moisturizer, and a combination of anti-dandruff, astringent, anti-inflammatory, and antibacterial agents [108,109]. Zn₂ is typically employed as a connecting point in nonlinear optically active MOFs to prevent undesirable d-d transitions in the visible region.

Recent research (Kitagawa et al. 2004; Rezwani et al. 2006; Ye et al. 2015) have highlighted the potential biological and medical applications of Zn-based MOFs as useful drug delivery vehicles and nontoxic/biocompatible medicinal agents [110,111]. Drugs could be encapsulated by MOFs and released gradually through their pores [112]. The therapeutic molecule was inserted directly as an organic constituent of the MOF framework in biocompatible drug carriers to prevent side effects [108,113]. Zinc-based MOFs with the aforementioned characteristics, together with low toxicity, biodegradability, and diverse functionality, can be thought of as excellent candidates for creating nanoencapsulators and achieving controlled drug release using cutting-edge delivery methods. According to Bahrani et al., [108], the benign metal Zn and low toxicity linkers carboxylate or phthalate were used to build up the available porosities in these materials.

The nature of host-guest interactions and pore properties have a significant impact on how well drug delivery systems operate in physiological media [114,114].

Deferiprone treatment for hemosiderosis can be seen as a promising ligand in bioactive Zn-based MOFs, as revealed by Burrows et al. [116]. Deferiprone as a chelating agent may be contained in the MOF's tri-zinc secondary structure before being released into the PBS. As shown by Sun et al. [117], the stiff scaffold provided by the bidentate carbene ligand makes Zn-MOF an effective carrier for the release of cisplatin, an effective anticancer agent with in vitro cytotoxic effects for ovarian cancer cells A2780. This MOF's structure is based on the bridging and chelating ligands 1,4-diazabi-cyclo [2.2.2] octane (DBCO) and 1,4-benzenedicarboxylic acid (H₂bdc), respectively. By using the MTT assay, the IC₅₀ value and cytotoxicity of MOF for human hepatoma cell (HuH₇) were found to be 1.0 mg/mL [108].

4.6. Environmental remediation

For the removal of heavy metals and contaminants from soil and air, MOFs have been proposed. In accordance with the World Water Development Report 2020, 1.6 billion people do not have access to clean water [118]. Additionally, the inclusion of extremely harmful compounds is fast lowering the quality of water supplies. Hazardous substances like dyes, insecticides, phenolics, and chlorinated chemicals are released due to anthropogenic activities like agriculture and industry.

In addition, routine activities have been introducing new pollutants such medications, personal care items, and hormone disrupting substances in minute amounts. The ecosystem may be seriously threatened by these harmful and cancer-causing micropollutants [119,120]. The rising need for fossil fuels like coal, oil, and natural gas is linked to another top-priority environmental concern. Uncontrolled burning of fossil fuels results in the release of harmful and offensive gases, such as volatile organic compounds and volatile sulfur-organic compounds, as well as CO_x, NO_x, and SO_x. These gases cause the air quality to significantly deteriorate and are either directly or indirectly related to acid rain and global warming [121,122]. Heterogeneous photocatalysis is a successful method for removing organic pollutants, and semiconductors like TiO₂, ZnO, and ZnS continue to be the most widely used options. Due to their wide band gap energy (Eg * 3.2–3.7 eV) and poor material recovery, these photocatalysts have some important limitations, including limited solar activity [123-125].

As several 3d-block transition metals' oxides and sulfides are known to have small bandgap energies (1.11 eV for CoFe₂O₄), they can be used to capture the complete UV-visible spectrum of the sun (Gupta et al. 2020c). As photocatalysts, MOFs with the metal centers Zn(II), Cu(I)/Cu(II), Co(II)/Co(III), and Fe(II)/Fe(III) enable the degradation of organic pollutants under UV/visible light. By transferring charge from the ligand to the metal cluster, the organic linkers in the MOF structure can serve as light "receptionists," activating the transition metal centers.

In photo-redox reactions, the excited MOF can generate electron-hole pairs that can be transported to the surface. The poor coordination of d-block transition metals with ligands in MOFs facilitates the formation of coordination vacancies where the coordinatively unsaturated metal centers act as Lewis acid catalytic sites [126]. Moreover, conjugated organic linkers could be used to adjust the light-harvesting characteristics of these coordinated polymers. The MOFs are regarded as the next generation of photocatalysts since they can utilize the full solar spectrum. Since gas collection and storage was one of MOFs' initial uses, it is possible to employ MOFs as adsorbents or catalysts to remove harmful gases, which could prove to be an efficient and direct method of reducing the rising level of air pollution.

On the other hand, municipal and industrial wastewaters are disposed of directly into pure water sources without any preparation, thereby introducing a variety of harmful organic compounds. By collecting and decomposing these contaminants into non-toxic chemicals, metal-organic frameworks (MOFs) are gaining attention as a viable alter-

native to lessen their negative effects on human health. In order to purge organic pollutants, innovative adsorbents and photocatalysts have been developed using these coordination polymers [127]. The most recent reports on MOFs for wastewater treatment, which are mainly concerned with the elimination of organic contaminants, have been provided in the subsections that follow. The efficacy of MOF-based photocatalysts for the degradation of organic colors, medicinal medicines, insecticides, and phenolic compounds is extremely investigated [128,129]. MIL-53(Fe) was reported by Xiang et al. (2017) for the removal of carbamazepine and clofibric acid from deionized water, sewage treatment plants, and river water. Inhibiting metabolism, reproduction, and embryonic development, these substances are medications used to treat excessive blood cholesterol levels and epilepsy, respectively. In 270 minutes, the metal-organic framework (MOF)/H₂O₂/visible system decomposed clofibric acid and carbamazepine, respectively, in 98.2 and 90.1% (deionized water), 94 and 88% (river water), and 71 and 86% (municipal wastewater) [130]. In addition to delayed kinetics and the need for a very low operational pH of 3, the process produced by-products that resembled humic acid and fulvic acid and needed extra treatment to be completely removed from water [130].

The in situ production of reactive species (OH, O²⁻), which are capable of mineralizing phenolic pollutants even at low concentrations, could be accomplished by heterogeneous photocatalysts using solar energy [131].

The use of metal-organic frameworks (MOFs) as photocatalysts for the degradation of pollutants was first proposed by Garcia's research team [132]. The metal ions in the scaffold are assumed to be responsible for the photocatalytic activity, while the organic linkers operate as light-absorbing chromophores that can gather photons from a wide range of the solar spectrum. When comparing the moles of phenol destroyed per metal ion in the material, MOF-5 displayed comparable photocatalytic activity to commercial TiO₂ P₂₅ and ZnO [133].

5. Conclusion and Future Prospects

Significant progress has been made in the introduction of MOFs as effective catalysts for gas separation, medical needs, and as remediation agents for pollution.

The enormous porosity and tunable structure of MOFs enable heavy loadings of biological molecules. But important factors including stability, toxicity, and biocompatibility may limit MOFs' performance in biomedical applications.

The antibacterial activity and biocompatibility of MOFs can be improved, making them a suitable material for medical devices that might greatly enhance healthcare features.

Describe how MOFs can be functionalized and modified with other nanomaterials to improve their separation capabilities, increase their sensitivity, and improve their selectivity when utilized in sensing applications.

The unique property of MOFs, when compared to other cutting-edge materials, is that their separation performances are unaffected by the presence of moisture, strongly indicating their potential for use in practical industrial applications such as water desalination, water purification, and gas storage.

These MOF adsorbents are predicted to play a significant role in the field of CO₂ capture if enhanced, as their high stability will improve their resistance to minor components (SO_x and NO_x) in flue gas as well as decreases in their regeneration energies and enormous synthesis costs.

The availability, affordability, kinetics of toxic gas adsorption/desorption, reusability, and long-term stability of MOFs toward such corrosive gases are significant practical challenges that need to be addressed.

Researchers have created these MOF-based catalysts that work incredibly well in polymerization reactions by utilizing their intrinsic porosity and the ability to synthesize them to create single-site catalysts with clearly defined structural properties.

Due to their relative young within this sub-field, these MOF polymerization catalyst materials have not yet achieved commercialization and use in industrial processes; nonetheless, MOF materials have in general achieved commercialisation. Given the recent commercial success of MOF materials, their potential application has a promising future because they can compete in activity and selectivity with present industrial catalysts.

Future research should examine how the MOF catalyst's physical characteristics vary and what impact those variations have on chemical synthesis of the MOF-based composites using in-situ techniques such as IR spectroscopy, Raman, X-ray absorption and so on.

In the near future, it is strongly advised to understand the catalytic mechanism of MOFs in order to have a clear understanding of how to optimize the reaction parameters and conditions for improved performance in chemical synthesis, including separation, polymerization, and biofuel production.

MOFs frequently have drawbacks that restrict their use, such as weak mechanical strength, poor stability, and a single function. Depending on the intended application, combining MOFs with particular materials is strongly advised.

The oxidation of functional groups or metal nodes during the synthesis processes, which can both result in the collapse of the micropores, may cause MOF structures to deteriorate after the compounding process. Such problems may be resolved, at the very least, by optimizing the synthesis settings and conditions or utilizing eco-friendly synthesis techniques.

Additionally, the maximum loading of metal ions in emerging moisture filtering and ion exchange techniques limits the number of NPs in MOF composites. The amount of metal ions loaded for initial wetness filtering depends on the solubility of the precursors in solution and the duration spent immersing the MOF powders, while the maximal loading for an ion-exchange method is determined by the number of active sites in MOFs. As a result, one of the primary difficulties in the synthesis of metal NP/MOF composites is to increase the metalNP loading while preventing their simultaneous aggregation in MOFs.

The production of high-quality MOF-based composites depends on the size, dispersion, and interactions of the MOF particles in the matrix.

The capacity of the membranes to separate will be enhanced by the great homogeneity and dispersion of MOF particles. As a result, there is a considerable demand for MOF particles with surface functionalization and size tuning. However, this research is still in its infancy, so more work needs to be done in the future. The synthesized MOF composites exhibit improved gas absorption, separation, storage capability, and catalytic capabilities thanks to the combination of MOFs and other functional species. Additionally, the interaction of functional elements and matrix materials with MOF structures can expand the uses of MOF composites in new industries including fuel cells, electrical catalysis, and drug delivery and release.

Though it has been asserted that MOFs are stable over a large pH range, there aren't many instances of this, therefore it's impossible to generalize and apply this to all MOFs. Along with the reusability, their durability against oxidants and radiation sources must also be taken into consideration.

A barrier to the commercialization of synthesized nanoscale MOF crystals for wastewater treatment may be the use of hazardous heavy metals (Cd, Cr, and Co), organic linkers (4,4-bipyridine and trimesic acid), solvents (N,N-dimethylformamide, chloroform, and acetone), and potential toxicity of the crystals (Kumar et al. 2019).

The price of manufacturing MOFs is another topic that is frequent-

ly overlooked in these research studies. It is difficult to evaluate and compare the cost-to-performance ratio with other traditional materials because there is no reliable estimate of the manufacturing cost of MOF.

The least hazardous transition metals, including Fe and Zn, can be given priority, even though it is not possible to limit the amount of organic linkers used in MOF production. Furthermore, by using solvent-free synthesis, hazardous solvents can be completely eliminated. Following alternative solvent-free routes could lower the cost of production because the synthesis of MOF through solvent-free methods like liquid-assisted grinding and aqueous synthesis is comparably less expensive (\$13–36 kg⁻¹) than organic solvent (solvothermal) synthesis (\$35–71 kg⁻¹) (DeSantis et al. 2017).

The practical application of MOFs necessitates a thorough comprehension of the chemical pathways and their applicability in actual wastewater, both of which should be thoroughly investigated before making any generalizations about their applicability in wastewater treatment facilities.

It is difficult to compare the benefits of adsorption versus catalysis, despite the fact that a small number of papers are devoted to analyzing the reusability difficulties.

MOFs are adaptable catalysts for air purification because they can selectively catalyze the reduction of NO with NH₃ or thermally degrade volatile organic sulfur compounds to produce S₈. Even though MOFs have several advantages for removing gaseous pollutants, they are thermally unstable and start to break down at temperatures as low as 300–400 °C. The thermal stability of MOFs can be improved by increasing the coordination forces with a proper choice of organic linkers and metal nodes.

Additionally, the hydrophilic nature of MOF metal nodes, particularly those that contain transition metals, reduces the active site density and jeopardizes structural integrity through hydrolysis processes. By selecting hydrophobic linkers and grafting oleophilic functions onto the open metal sites, it is possible to create hydrophobic MOFs that will perform better by preventing the entry of water molecules.

Additionally, the MOF stability should be assessed by preserving MOFs in various atmospheric settings to observe how MOFs degrade in the presence of atmospheric oxygen (Du et al. 2019).

Overall, it appears that military applications will more likely lead to MOF commercialization than civilian ones. Every conceivable premise for the commercialization of MOFs is based on their low cost of production, great efficacy, and lack of dependence on secondary chemicals or processes. Therefore, finding inexpensive precursors is crucial for an efficient way to manufacture MOF.

A cost-saving solution could be to locate the least-costly way to produce a MOF instead of using a multi-step procedure.

Another persuasive argument against using MOFs in the wastewater treatment process might be made by doing a more thorough assessment of MOF toxicity to people and other living things. Although the current development of MOFs for environmental applications is constrained by a lack of understanding, MOFs' future importance is very certain. We predict that transition metal-based MOFs will replace current adsorbents and catalysts in commercial air and gas decontamination operations in the next years.

The ability of the synthesis method to be scaled up from an academic/laboratory setting to a big industrial one will determine the future of MOFs. The different factors that should be considered while developing industrial MOF production processes include cost, raw material availability, technical simplicity, yields, purity and quality of synthesized MOFs, and environmental impact. The space-time yield of the synthesis reaction is frequently used to assess the effectiveness of a selected approach. The mass of a MOF produced in one day of synthesis, expressed in kilograms per cubic meter of the reaction mixture, is known as the space-time yield.

For producing MOFs on a wide scale, techniques with high space-time yield values are thought to be the most effective. The literature has discussed the space-time yield values of popular MOFs synthesized utilizing various procedures (Rubio-Martinez et al. 2017). For environmental applications, it makes little sense to produce materials with a high environmental imprint. Because of this, before commercializing the process, factors like environmental footprint should be taken into account in addition to variables like space-time yield.

Commercial MOFs made by Badische Anilin und Soda Fabrik, MOF Apps, and MOF Technologies, including HKUST-1, MOF-5, UiO-66 series, ZIF-67, and ZIF-8, are offered by Sigma-Aldrich (Rubio-Martinez et al. 2017).

The main barrier keeping MOFs from displacing traditional adsorbents in environmental applications is their high cost as of yet. But as the industry develops, new players are joining the market to sell less well-known MOFs, and they'll undoubtedly offer MOFs up to their use in practical environmental applications.

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Conflicts of interest

All authors declare no conflicts of interest in this paper.

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