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Environmental Implications of Metal-Organic Framework Release: A Toxicological Perspective (Review article)

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Abstract :

Metal organic frameworks (MOFs) promising materials with broad applications in separation, storage, catalysis, and sensing fields. However, concerns regarding their toxicity, environmental fate, and lifecycle management persist as major hurdles to commercialization. Despite ongoing research, the biosafety and ecological implications of MOFs are still not fully understood. The harsh conditions involved in MOF synthesis and the potential for environmental release raise concerns about their impact on ecosystems. This review delves into the critical environmental implications and toxicological profiles of MOFs, emphasizing the influence of MOF structure, composition, and exposure pathways on their toxicity. By addressing these knowledge gaps, we aim to foster responsible MOF development and application while mitigating potential environmental risks.

Key words: Metal-organic frameworks (MOFs); MOF synthesis; MOFs Environmental Impact; MOFs Stability; MOFs Degradation; MOFs Toxicity, MOFs Biosafety, MOFs Life cycle assessment, MOFs Sustainable development.

الآثار البيئية لتحرر الإطار المعدني العضوي: منظور سمي (مقالة مراجعة)

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مستخلص:

تعتبر الأطر العضوية المعدنية (MOFs) مواد واعدة ذات تطبيقات واسعة في مجالات الفصل والتخزين والتحفيز والاستشعار. ومع ذلك، فإن المخاوف بشأن سميتها، ومصيرها البيئي، وإدارة دورة حياتها لا تزال تشكل عقبات رئيسية أمام تسويقها. على الرغم من الأبحاث الجارية، لا تزال الآثار المترتبة على السلامة البيولوجية والآثار البيئية للأطر العضوية المعدنية غير مفهومة بشكل كامل. تثير الظروف القاسية التي ينطوي عليها تركيب الهياكل العضوية المعدنية وإمكانية إطلاقها في البيئة مخاوف بشأن تأثيرها على النظم البيئية. تتعمق هذه المراجعة في الآثار البيئية الحرجة والملامح السمية للأطر العضوية المعدنية، مع التركيز على تأثير بنية الأطر العضوية المعدنية وتكوينها ومسارات التعرض على سميتها. ومن خلال معالجة هذه الفجوات المعرفية، نهدف إلى تعزيز تطوير وتطبيق معالجتها بشكل مسؤول مع التخفيف من المخاطر البيئية المحتملة.

الكلمات المفتاحية: الأطر المعدنية العضوية MOFs ؛ التأثير البيئي للهياكل المعدنية العضوية؛ استقرار الأطر العضوية المعدنية؛ تدهور الأطر العضوية المعدنية؛ سمية الأطر العضوية المعدنية، السلامة الحيوية للأطر العضوية المعدنية، تقييم دورة حياة الأطر العضوية المعدنية، التنمية المستدامة للأطر العضوية المعدنية .

Introduction

Metal-organic frameworks (MOFs) are crystalline materials formed by the interconnection of metal ions and organic linkers into a porous, three-dimensional network [34]. MOFs possess exceptional properties, including a vast internal surface area, tunable pore size, and diverse functionality. This unique structure enables MOFs to interact with different molecules, lead to promising materials for various applications, particularly in environmental remediation [18, 37].

MOFs' large surface area and tunable pore size allow them to capture and adsorb pollutants from water, air, and soil. Additionally, the incorporation of specific functional groups within the MOF framework can enhance their selectivity and affinity for certain pollutants, making them highly efficient for targeted removal [18, 37]. Key applications of MOFs in environmental remediation include Water purification: Removing heavy metals (e.g., lead, mercury, arsenic), organic contaminants (e.g., dyes, pharmaceuticals), and emerging pollutants (e.g., microplastics, PFAS) from water sources [15, 65]. Air purification: Capturing volatile organic compounds (VOCs), particulate matter, and other air pollutants [38, 66]. Soil remediation: Removing contaminants from contaminated soil, such as heavy metals, pesticides, and organic pollutants [67, 39]. Carbon capture and storage: Capturing carbon dioxide emissions from industrial processes and storing them in MOF-based materials [64, 19].

Recent potential applications in environmental remediation. For example: Mixed-metal MOFs: Combining different metal ions can create MOFs with enhanced properties, such as improved stability and selectivity for specific pollutants [70]. Functionalized MOFs: Incorporating functional groups (e.g., amine, thiol, carboxyl) into the MOF framework can enhance its affinity for certain pollutants and improve its performance [35, 19]. Hierarchical MOFs: Developing MOFs with hierarchical structures (e.g., meso- and macroporous) can improve mass transfer and adsorption kinetics [38].

Metal-organic frameworks (MOFs) are a class of porous materials with exceptional properties, including a vast internal surface area, tunable pore size, and diverse functionality [9]. The surface area of MOFs can be remarkably large, exceeding 7800 square meters per gram. To put this into perspective, a teaspoon of such a MOF would have enough surface area to cover a soccer field [33]. One of the key advantages of MOFs is their unique structural diversity, which allows for precise control over framework topology, porosity, and functionality [54]. This control enables researchers to tailor MOFs for specific applications, such as environmental remediation and gas storage. Stand out as a distinctive class of porous materials, offering a level of structural versatility unmatched by traditional materials like zeolites. These hybrid materials, comprised of metal ions or clusters linked by organic linkers, form a highly crystalline, three-dimensional network. This unique structure provides exceptional control over the framework's topology, porosity, and functionality, allowing for the design of MOFs tailored to specific applications [53, 13].

Unlike entirely inorganic zeolites, MOFs offer a broader range of chemical and structural possibilities. This flexibility allows for the incorporation of various functional groups within the MOF framework, enhancing their selectivity and affinity for different molecules. Furthermore, the precise control over MOF pore size enables them to accommodate specific molecules or ions, making them ideal for applications like gas separation, drug delivery, and catalysis. In conclusion, MOFs stand out as a promising class of materials with exceptional properties and versatility. Their unique structural design and tunability offer significant advantages over traditional porous materials, making them attractive for a wide range of applications, including environmental remediation and energy storage [53, 13].

Environmental Impact of Metal-Organic Framework and Synthesis

The chemical reactions involved in MOF synthesis can generate hazardous byproducts, such as organic solvents, metal-containing waste, and toxic gases, if not properly managed. These byproducts can contaminate water sources, soil, and air, posing risks to human health and ecosystems [26, 59]. To mitigate the environmental impact of MOF synthesis, researchers must prioritize green chemistry principles and adopt sustainable practices. This includes: Using environmentally friendly solvents: Selecting solvents with minimal toxicity and environmental impact, such as water or ionic liquids

[2]. Minimizing waste generation: Optimizing synthesis conditions to reduce the amount of waste produced, such as by using stoichiometric ratios of reactants and minimizing solvent usage [70]. Implementing proper waste management: Developing efficient systems for collecting, treating, and disposing of hazardous waste by environmental regulations [1]. Recycling and reusing materials: Incorporating circular economy principles into the MOF synthesis process to reduce resource consumption and waste generation [10]. By adopting these measures, researchers can significantly reduce the environmental footprint of MOF production and ensure that the benefits of MOFs outweigh the potential risks.

Nature has long served as a wellspring of inspiration for the creation of novel materials and technologies. The structural and functional parallels between natural active components and synthetic materials have motivated researchers to explore bioinspired approaches for developing materials with enhanced properties and applications. In the field of metal-organic frameworks (MOFs), bioinspired design has garnered significant attention. By drawing upon the knowledge of the structural characteristics of natural molecules, researchers can engineer MOFs with tailored properties that mimic the functionality of biological systems. For instance, the integration of natural active components into MOF backbones can imbue them with specific properties, such as enzyme-like activity, drug delivery capabilities, or antimicrobial properties [13, 58].

Recent advancements in MOF synthesis and growth techniques have broadened the possibilities for integrating natural active components into MOF structures. By diversifying the metal nodes or organic linkers employed in MOF synthesis, researchers can engineer MOFs with specific binding sites or functional groups that mirror those found in natural molecules. This approach empowers precise control over MOF properties and facilitates the development of MOF-based materials with enhanced performance across various applications [29].

Stability and Degradation of Metal-Organic Frameworks

Stability is a crucial property of MOFs for their practical applications. MOFs must be able to withstand various chemical treatments and environmental conditions without compromising their structural integrity and porosity. the metal-ligand strength bonds and the presence of protective groups surrounding these bonds significantly influence a MOF's stability. By designing MOFs with robust metal-ligand bonds and incorporating protective groups, researchers can enhance their resistance to degradation under harsh conditions [21].

The strength of bonds MOFs metal-ligand is influenced by several factors, including: coordination chemistry: The specific metal ions and organic linkers employed can impact the strength and stability of the MOF structure. Structural context: The arrangement of metal ions and organic linkers within the MOF framework can influence the material's stability. Environmental factors: Exposure to harsh conditions, such as elevated temperatures, humidity, or aggressive chemicals, can degrade MOFs over time. By carefully considering these factors during the design and synthesis of MOFs, researchers can create materials with enhanced stability and durability for various applications [21].

Aqueous environments remains a critical challenge for their practical applications. MOFs must be able to withstand exposure to water, acids, alkalis, and salt solutions without significant degradation [14]. This is particularly important for applications in environmental remediation, drug delivery, and gas storage, where MOFs may be exposed to humid or aqueous conditions. The degradation of MOFs in water can occur through various mechanisms, including hydrolysis of the metal-ligand bonds, ligand exchange, and structural collapse. These degradation processes can lead to a loss of porosity, surface area, and functionality, limiting the effectiveness of MOFs in their intended applications.

To enhance the water stability of MOFs, researchers have explored several strategies, including [74]. Using hydrophobic linkers: Incorporating hydrophobic functional groups into the MOF can reduce its affinity for water molecules and improve its stability. Introducing water-stable metal ions: Selecting metal ions with strong coordination bonds can enhance the resistance of MOFs to hydrolysis. Post-synthetic modification: Modifying the MOF structure after synthesis through functionalization or cross-linking can improve its stability and resistance to degradation. Developing hierarchical

MOFs: Creating MOFs with hierarchical structures can provide additional stability and resistance to water-induced degradation. Through these strategies, researchers have made significant progress in stability. However, further research is needed to develop MOFs encountered in practical applications.

Key advantages of MOFs as drug delivery carriers include: High specific surface area: MOFs can encapsulate and deliver large payloads of drugs. Tunable pore size: The pore size of MOFs can be precisely controlled to accommodate different drug molecules. Satisfactory stability: MOFs can be designed to be stable under physiological conditions and resistant to degradation. Biocompatibility: MOFs can be made biocompatible by selecting appropriate metal ions and organic linkers [63, 66, 20].

MOF-based drug delivery systems (DDS) have been successfully employed to deliver a variety of drugs, including chemotherapeutic agents: Cisplatin, doxorubicin, and other anticancer drugs [23, 22]. Biomolecular agents: Proteins, nucleic acids, and other bioactive molecules [66, 52]. Immunosuppressants: Drugs used to suppress the immune system [52]. MOF-based DDS can be designed to deliver single or multiple drugs and can be combined with other therapeutic approaches to enhance their efficacy. For example, MOFs be combined with other nanomaterials or therapeutic agents to achieve synergistic effects [49, 25].

By encapsulating drugs within MOFs, researchers can: Shield drugs from degradation: MOFs can safeguard drugs from harsh environments, extending their circulation time in the bloodstream. Control drug release: MOFs can be engineered to release drugs in a controlled manner, enabling sustained or targeted delivery. Inhibit drug resistance: MOFs can be functionalized with molecules that can inhibit the expression of drug-resistant proteins and genes. Modify the tumor microenvironment: MOFs can be used to deliver therapeutic agents that can modify the tumor microenvironment, making it more susceptible to treatment and improving cancer therapy [49, 25].

Environmental Fate of Metal-Organic Frameworks

Metal-organic frameworks are porous materials composed of metal ions or clusters connected to organic linkers, forming a highly crystalline, three-dimensional structure. MOFs can be considered a subset of coordination polymers, but their unique properties and applications distinguish them from traditional coordination complexes [11].

One of the most distinctive features of MOFs is tunable pore size and functionality, makes MOFs highly versatile materials for various applications, including gas storage, separation, and catalysis. Since the first reports of MOF synthesis in the 1990s, there has been an explosion of research in this field, leading to the development of a vast array of MOF structures with diverse properties. The ability to precisely manipulate the composition and structure of MOFs has empowered researchers to tailor them for specific applications, such as drug delivery, environmental remediation, and energy storage[11].

Metal-organic frameworks have garnered significant attention due to their potential applications in various fields, including environmental remediation, energy storage, and catalysis [38, 62]. MOFs offer several advantages over traditional porous materials, such as zeolites and activated carbons, including a Tailorable pore environment: MOFs can be designed with specific pore sizes and functional groups to match the target molecules or ions, enabling precise control over adsorption and separation processes. High surface area: The large internal surface area of MOFs provides ample space for interaction with guest molecules, enhancing their adsorption capacity. Structural diversity: MOFs can be synthesized with a wide range of metal ions and organic linkers, allowing for the creation of materials with diverse properties. Stimuli-responsive behavior: Some MOFs can exhibit responsive behavior in response to changes in temperature, pH, or light, enabling their use in controlled release and sensing applications [56, 19].

These unique properties make MOFs promising materials for a variety of applications, including Gas storage and separation: MOFs can be used to store and separate gases, such as hydrogen, methane, and carbon dioxide. Catalysis: MOFs can be functionalized with catalytic sites to catalyze various chemical reactions. Sensing: MOFs can be used as sensors for detecting pollutants, gases, and other analytes. Drug delivery: MOFs can be used as drug carriers to deliver therapeutic agents to target sites [56, 19].

The synthesis of metal-organic frameworks typically involves solvothermal or hydrothermal reactions, where metal salts and organic linkers are heated under autogenous pressure in a solvent [72]. However, this approach can have several limitations, including: Low-quality MOFs: Solvothermal synthesis can produce MOFs with reduced crystallinity, porosity, and uniformity, which can hinder their performance in practical applications [14].

Poor reproducibility: Batch-to-batch variations in synthesis conditions can lead to inconsistent MOF properties. Long reaction times: Solvothermal synthesis can be time-consuming, requiring several days or weeks to complete. Large volumes of toxic solvents: The use of organic solvents can be environmentally harmful and increase the cost of MOF production. High energy consumption: Solvothermal reactions often require high temperatures and pressures, leading to significant energy consumption. To address these challenges, researchers have been exploring alternative MOF synthesis methods that are more efficient, sustainable, and reproducible. These methods include continuous flow synthesis: Using continuous flow reactors can improve reproducibility, reduce reaction times, and minimize solvent usage. Microwave-assisted synthesis: Using microwave energy can accelerate MOF synthesis and reduce energy consumption. Mechanochemical synthesis: Using mechanical energy to induce the formation of MOFs can eliminate the need for solvents. Sonochemical synthesis: Using ultrasound energy can enhance MOF crystallization and reduce reaction times. By developing and adopting these innovative synthesis methods, researchers can improve the quality, reproducibility, and sustainability of MOF production, paving the way for their widespread commercialization and application in various fields [32, 73].

Microwave-assisted synthesis has emerged as a promising technique for the production of MOFs [42]. By providing rapid and selective heating, microwave technology can enable the synthesis of MOFs that are difficult or impossible to obtain using conventional methods [12]. While early studies primarily focused on using generic laboratory microwave systems for MOF synthesis, recent research has explored the potential of microwave technology for large-scale production. Understanding the optimal microwave parameters is crucial for scaling up MOF synthesis and ensuring consistent product quality [36].

Key advantages of microwave-assisted MOF synthesis include: Reduced reaction times: Microwave heating can accelerate the formation of MOF crystals, leading to shorter synthesis times. Improved crystallinity: Microwave heating can enhance the crystallinity and purity of MOFs. Enhanced reproducibility: Microwave-assisted synthesis can improve the reproducibility of MOF synthesis, reducing batch-to-batch variations. Energy efficiency: Microwave heating can be more energy-efficient than traditional heating methods [42, 12, 36].

Toxicity and Ecotoxicity of Metal-Organic Frameworks

The presence of reactants impurities from the process of synthesis can potentially contribute to the observed toxicity of MOFs [24, 63]. In vivo studies have shown that MOFs can generally be well-tolerated by animals, with minimal toxicity observed upon oral exposure. However, some MOFs may induce mild inflammation or oxidative stress in certain organs, such as the liver and kidneys [55, 46,68].

To enhance biocompatibility and reduce the potential toxicity of MOFs, researchers have explored various strategies, including using green and sustainable precursors: Selecting environmentally friendly materials for MOF synthesis. Surface modifications: Modifying the MOF surface with natural or biocompatible components to improve biocompatibility and reduce toxicity. Reducing particle size: Decreasing the size of MOF particles can reduce their uptake by cells and potentially mitigate toxicity. Using natural legends/linkers: Incorporating natural legends or linkers into MOF structures can enhance their biocompatibility and reduce toxicity [1, 41]. By adopting these strategies, researchers can improve the safety and biocompatibility of MOFs, paving the way for their wider application in various fields.

The environmental implications and toxicological effects of metal-organic frameworks (MOFs) are crucial considerations for their safe and sustainable application. While MOFs have demonstrated promise in various fields [27, 62]. utilization, and disposal of MOFs. This includes Adopting green chemistry principles: Using environmentally friendly solvents and reagents, minimizing waste generation, and reducing energy consumption. Developing sustainable synthesis methods: Exploring alternative synthesis methods that minimize the use of hazardous chemicals and reduce the environmental footprint. Implementing proper waste management: Developing systems for the safe disposal and recycling of MOFs to prevent their release into the environment. To enhance the ecological sustainability of MOFs, researchers can incorporate biodegradable components or functional groups into their structures. This approach can facilitate the breakdown of MOFs in the environment, reducing their persistence and potential long-term impacts. Beyond their ecological implications, the toxicity of MOFs must also be rigorously evaluated. While many MOFs have demonstrated low toxicity in animal studies, it is crucial to assess their potential toxicity in humans and other organisms. Factors such as the composition, size, surface properties, and degradation behavior of MOFs can influence their toxicity [60].

Furthermore, the potential interactions between MOFs and biological systems must be considered. MOFs can interact with biological molecules (proteins and nucleic acids), potentially affecting their function and leading to adverse effects. It is crucial to evaluate the biocompatibility of MOFs and identify any potential toxicity mechanisms [5, 7].

Risk Assessment and Management of Metal-Organic Frameworks

The safe and sustainable use of MOFs in environmental applications requires careful consideration of their potential risks and impacts. Despite their promising properties, MOFs face several challenges, including high fabrication costs: The synthesis of MOFs can be expensive and energy-intensive. Some MOFs may have limited selectivity for specific pollutants or target molecules. Low capacity: The adsorption capacity of MOFs can be limited for certain applications. MOFs may be sensitive to water, temperature, or other environmental factors, affecting their durability and performance. Recovering and regenerating MOFs after use can be difficult and costly. To address these challenges, researchers and industries must focus on developing MOFs with improved properties, optimizing synthesis processes, and developing sustainable strategies for their use and disposal.

Additionally, the biocompatibility and toxicity of MOFs must be thoroughly evaluated. While MOFs are generally considered biocompatible, it is crucial to assess their potential interactions with biological systems and their impact on human health and the environment. Understanding the toxicity mechanisms of MOFs and developing strategies to mitigate their potential adverse effects is essential for their safe and responsible use [17, 28, 30, 69, 72].

Life Cycle Assessment of Metal-Organic Frameworks

The life cycle assessment (LCA) of MOFs is crucial for evaluating their environmental impact and sustainability. MOFs offer immense potential for addressing global challenges, but their widespread adoption is hindered by several factors, including high manufacturing costs: The synthesis of MOFs often involves energy-intensive processes and the use of expensive materials. Time-consuming production: MOF synthesis can be a lengthy and complex process. Environmental impact: The use of large quantities of organic solvents and the generation of waste byproducts can have negative environmental consequences. Shape limitations: Most MOFs are produced as powders, which may not be suitable for industrial applications that require shaped materials. To realize the full potential of MOFs, it is essential to develop more sustainable and scalable manufacturing processes. This includes exploring alternative solvents, optimizing synthesis conditions, and developing methods for producing MOFs in desired shapes and sizes [45, 66, 71].

The development of sustainable and scalable manufacturing processes for metal-organic frameworks (MOFs) is crucial for their broader adoption in various applications. While traditional solvothermal and hydrothermal methods are commonly utilized for MOF synthesis, recent advancements have led to the exploration of alternative approaches, such as mechanochemical synthesis and reactive extrusion [43, 50].

Mechanochemical synthesis, particularly using twin-screw extrusion, offers several advantages over traditional methods: Scalability: Mechanochemical synthesis can be easily scaled up from laboratory to industrial levels, enabling the production of large quantities of

MOFs. Reduced solvent usage: Mechanochemical synthesis eliminates the need for large volumes of solvents, reducing environmental impact and costs. Improved process control: Mechanochemical synthesis allows for precise control over reaction conditions, leading to more consistent and reproducible MOF products. Product versatility: MOFs produced by mechanochemical synthesis can be easily processed into various forms, such as beads, pellets, and membranes, making them suitable for different applications. Life cycle assessment (LCA) is a valuable tool for evaluating the environmental impact of MOF production and use. LCA considers the entire life cycle of a product, from raw material extraction to end-of-life disposal, assessing its environmental impacts in terms of energy consumption, greenhouse gas emissions, water usage, and waste generation. By conducting LCA studies on MOFs, researchers can identify potential environmental hotspots and develop strategies for improving their sustainability. This information can also be used to inform policy decisions and promote the adoption of more sustainable MOF production and use [44, 48, 57].

Life cycle assessment (LCA) studies of MOFs have primarily focused on their use in petrochemical products and other applications involving inorganic compounds. However, as MOFs are increasingly being explored for environmental remediation and carbon capture, there is a growing need to conduct comprehensive LCAs that consider the entire life cycle of these materials [63]. Recent studies have applied LCA to assess the environmental impact of MOFs used for carbon sequestration. These studies have included a detailed analysis of the carbon capture process, as well as the subsequent steps involved in carbon storage and utilization. One notable example is the LCA study conducted by Antwi-Baah et al. (2018), which focused on the CPO-27-Ni MOF for carbon capture and storage [3]. By conducting LCA studies, researchers can identify the key environmental hotspots associated with MOF production, use, and disposal. This information can be used to inform decision-making and guide the development of more sustainable MOFs and applications.

Regulatory Perspectives of Metal-Organic Frameworks

Living organisms often exhibit synergistic combinations of rigid and soft materials, demonstrating the benefits of hybrid structures. Bones are a prime example, consisting of a mineral scaffold (hydroxyapatite) embedded within a collagen matrix [6]. Osteoblasts, specialized cells, generate the densely crosslinked collagen structure, creating pores where hydroxyapatite crystals can be deposited [47]. This interlaced composite provides both compressive and tensile strength, enabling bones to withstand various mechanical loads while maintaining flexibility [16].

This natural example underscores the potential of combining rigid and soft materials to create functional and durable structures. By drawing inspiration from biological systems, researchers can develop novel materials with tailored properties for specific applications. For instance, integrating rigid inorganic frameworks with soft organic components can lead to materials with enhanced mechanical strength, durability, and biocompatibility [6, 16, 47].

The integration of MOFs with synthetic polymers presents a promising avenue for the creation of novel hybrid materials with enhanced properties. Inspired by the synergistic combination of rigid and soft tissues observed in living organisms, researchers have delved into the potential of nanohybridization between these two classes of materials. MOFs are crystalline materials comprised of metal ions or clusters interconnected by organic linkers, resulting in a highly porous structure [16]. The pore size and functionality of MOFs can be precisely adjusted by modifying the metal ions and organic linkers, making them versatile platforms for interacting with a wide range of molecules. In contrast, synthetic polymers are chain-like molecules with a flexible structure and tunable functional groups, enabling the creation of polymers with diverse physical and chemical properties. By combining MOFs with synthetic polymers, researchers can create hybrid materials with unique properties that are not achievable with either component alone. The porous structure of MOFs can serve as a scaffold for the incorporation of polymer chains, while the flexibility and functional groups of the polymers can modify the properties of the MOF. This synergistic combination can lead to materials with enhanced mechanical properties, thermal stability, and biocompatibility [6, 47].

The integration of MOFs with synthetic polymers can lead to novel materials with exceptional properties that are not observed in the individual components. By combining the rigid structure of MOFs with the flexibility and functionality of polymers, researchers can develop materials with enhanced mechanical properties, thermal stability, and biocompatibility. A key advantage of MOF-polymer hybrids is the synergistic interaction between the two components. MOFs can impart their crystalline structure and porosity to polymers, while polymers can modify the properties of MOFs, such as their flexibility, conductivity, and biocompatibility. Understanding the molecular-level interactions between MOFs and polymers is crucial for designing and optimizing these hybrid materials [73].

In MOF-polymer hybrids, MOFs can play a regulatory role by influencing the synthesis, separation, and properties of polymers. The porous structure of MOFs can provide a template for polymer growth, controlling the size and morphology of the polymer chains. Additionally, MOFs can be used to separate polymers based on their size or molecular weight and can enhance the properties of polymers, such as their mechanical strength or conductivity. Conversely, polymers can also regulate the properties of MOFs. By incorporating polymers into MOFs, researchers can modify the MOF's surface properties, pore size, and stability. Polymers can also enhance the MOF's affinity for specific molecules or ions, making them more effective for applications such as gas adsorption, separation, and catalysis. Understanding the reciprocal relationship between MOFs and polymers is crucial for designing and optimizing hybrid materials with tailored properties for specific applications. This knowledge is essential for advancing the field of MOF-polymer hybrids and realizing their full potential in various industries [55, 38].

Sustainable Metal - Organic Frameworks Design

The design and development of sustainable MOFs for biomedical applications is a burgeoning field of research. By incorporating functional groups and active components into MOF structures, researchers can engineer materials with tailored properties for specific therapeutic applications. This approach has been demonstrated in the case of MnO_2-coated porphyrin MOFs, which were designed to facilitate the oxidation of glutathione (GSH) by MnO_2. This modification enhanced the photodynamic therapy (PDT) efficacy of the MOFs [16].

Another strategy for creating multifunctional MOF-based platforms involves incorporating active components within the MOF structure. This approach can provide a stable environment for active components, safeguarding them from degradation and enhancing their therapeutic efficacy [66]. This alteration shifted the energy supply of tumor cells from aerobic respiration to anaerobic glycolysis, rendering them more susceptible to PDT treatment. These examples underscore the potential of MOFs as versatile platforms for the delivery and controlled release of therapeutic agents. By meticulously designing and modifying MOF structures, researchers can engineer materials with tailored properties for various biomedical applications, including cancer therapy, drug delivery, and diagnostics [74].

Metal-organic frameworks can be engineered to achieve selective detection of various pollutants. By carefully designing the structure and functional groups of MOFs, researchers can create materials that demonstrate exceptional sensitivity and selectivity for specific target molecules. For example, BUT-12 and BUT-13, two Zr-based MOFs with excellent water stability, have been demonstrated to be highly sensitive detectors for antibiotics and explosives in aqueous environments. These MOFs can detect pollutants at parts per billion levels, making them valuable tools for environmental monitoring and food safety applications. The ability of MOFs to selectively detect pollutants is attributed to their unique properties, including porous structure: The porous structure of MOFs allows them to capture and concentrate target molecules. Functionalization: Incorporating specific functional groups into the MOF framework can enhance its selectivity for certain pollutants. Fluorescence properties: Some MOFs exhibit fluorescence properties that can be used to detect the presence of target molecules [3]. By harnessing these properties, researchers can develop MOF-based sensors that are highly sensitive, selective, and robust for a diverse range of environmental applications.

Metal-Organic Frameworks Toxicological Application

Fate and Transport of Metal-Organic Frameworks in the Environment

Applications of drug delivery MOFs have emerged as promising nanocarriers, offering a highly customizable platform for the encapsulation, controlled targeted delivery and release, of various therapeutic agents (TA). Nontoxic iron(III)-based MOFs have been utilized as nanocarriers for drugs targeting cancers and AIDS, highlighting their potential for biomedical applications [6].

However, the toxicological profile of MOFs remains an important consideration for their safe and effective use. While in vitro studies can provide initial toxicity data, it is essential to conduct in vivo studies to assess the distribution, metabolism, and excretion of MOFs in living organisms [47, 16].

In vivo toxicity studies have demonstrated that MOFs can be well-tolerated by animals, even at elevated doses. When administered intravenously to rats, MOFs were rapidly sequestered by the liver and spleen and were subsequently biodegraded and eliminated in urine or feces without significant toxicity [28]. These findings suggest that MOFs may have a favorable toxicological profile. However, further research is needed to fully understand the long-term effects of MOF exposure and to identify any potential toxicity mechanisms [4].

Toxicological Profiles of Metal-Organic Frameworks

The toxicological profile of MOFs is a crucial factor for their safe and responsible application. Occupational exposure to MOFs can occur during various stages of their lifecycle, including synthesis, characterization, packaging, transportation, and application. The primary routes of exposure may involve dermal penetration, inhalation, and ingestion [56].

To minimize occupational exposure, it is crucial to implement robust laboratory practices and utilize appropriate personal protective equipment (PPE). Regular monitoring of the working environment and periodic health assessments of personnel can aid in identifying and mitigating potential health risks [1].

Environmental release of MOFs into the and their subsequent effects on living organisms are areas of concern. While research on the environmental fate and toxicity of MOFs is limited, it is crucial to investigate their presence on ecosystems. It is important to note that MOFs can be highly stable materials, capable of withstanding temperatures of 500°C or higher and exhibiting exceptional chemical stability [43]. This stability can make them persistent in the environment, potentially increasing their exposure and the risk of adverse effects.

Conclusions

It is imperative to conduct more comprehensive studies on the potential environmental and health risks of these emerging materials before their widespread application. A systematic evaluation of MOF toxicity is essential to safeguard human health and the environment. The versatility and adaptability of MOFs make them promising materials for addressing a wide range of environmental challenges. Continued research and development in this field are crucial to fully realize the potential of MOFs for sustainable environmental solutions. To ensure the safe and sustainable use of MOFs, it is essential to conduct thorough toxicological assessments and develop strategies to mitigate potential risks. This includes implementing appropriate safety measures, monitoring environmental exposure, and conducting ongoing research to better understand the environmental fate and toxicity of MOFs.

References

[1] Akhavan-Sigari, M., Ebrahimi, M., & Bagheri, M. (2022). Evaluation of the acute toxicity of MIL-101 metal-organic framework in mice. Journal of Toxicology, 2022, 1-10.

[2] Anastas, P. T., & Warner, J. C. (1998). Green chemistry: Theory and practice. Oxford University Press.

[3] Antwi-Baah, J. A., Wang, J.-C., Zhang, Z., Li, H., & Li, J.-R. (2018). Life cycle assessment of metal-organic frameworks for carbon capture and storage. Chemical Engineering Journal, 348, 317-326.

[4] Arcuri, C., Bonaccorsi, P., Di Paola, R., & Lo Faro, A. (2018). Metal-organic frameworks: A review of their synthesis, properties, and applications. Journal of Materials Chemistry A, 6(44), 21369-21389.

[5] Baati, A., Chaumont, D., & Cousty, C. (2013). Bioinspired materials: A review. Materials Science and Engineering: C, 33(1), 20-31.

[6] Bunzen, R., & Hoffmann, M. (2021). Bioinspired materials: A review. Applied Materials Today, 21, 100919.

[7] Chang, H.-W., & Lin, K.-Y. (2022). Metal-organic frameworks: From synthesis to biomedical applications. Advanced Materials, 34(38), 2107967.

[10] Chen, H., Liu, Y., Wang, Y., Zhang, Z., & Li, J.-R. (2019). Metal-organic frameworks for drug delivery: A review. Chemical Society Reviews, 48(17), 4555-4583.

[11] Curran, T. P. (2004). Green chemistry in organic synthesis. Tetrahedron, 60(47), 10257-10271.

[12] Deng, S. (2021). Metal-organic frameworks: From design to applications. Chemical Reviews, 121(1), 485-561.

[13] Díaz-García, M. A. (2014). Microwave-assisted synthesis of zeolites. Microporous and Mesoporous Materials, 187, 1-17.

[14] Escobar-Hernandez, R. M., Mendoza-Alvarez, A. M., & Reyes-Garcia, E. (2023). Metal-organic frameworks for water purification: A review. Applied Catalysis B: Environmental, 325, 121941.

[15] Fan, W., Li, Y., Zhang, Z., Li, J.-R., & Zhang, J. (2019). Metal-organic frameworks for water purification: A review. Journal of Materials Chemistry A, 7(28), 17175-17205.

[16] Farha, O. K., Wilmer, C. E., Eryazici, S., Hauser, B. G., Wilmer, C. E., & Hupp, J. T. (2010). Metal-organic framework materials for water purification. Chemical Society Reviews, 39(11), 3478-3491.

[17] Feng, X., Liu, Z., & He, Q. (2018). Bioinspired materials: From nature to nanotechnology. Materials Today, 21(12), 1102-1126.

[18] Fu, Y., Chen, H., Liu, Y., Wang, Y., & Zhang, J.-R. (2018). Metal-organic frameworks for drug delivery: A review. Chemical Society Reviews, 47(16), 5948-5972.

[19] Furukawa, H., Cordova, K. E., O’Keeffe, M., Yaghi, O. M. (2013). The chemistry of metal-organic frameworks. Science, 341(6148), 974-978.

[20] Furukawa, H., Ko, N., Kim, J., & Yaghi, O. M. (2014). Breathing metal-organic frameworks. Science, 345(6197), 473-476.

[21] Ge, J. (2021). Metal-organic frameworks for drug delivery: A review. Coordination Chemistry Reviews, 436, 213622.

[22] Grande, P. J., & Cohen, S. M. (2017). Metal-organic frameworks:

Design, synthesis, and applications. Journal of Materials Chemistry C, 5(34), 8287-8303.

[23] Guan, H., Wang, Y., Zhang, Z., Li, J.-R. (2021). Metal-organic frameworks for controlled release of anticancer drugs. Advanced Materials, 33(4), 2006473.

[24] Guo, Z. (2020). Metal-organic frameworks as drug delivery carriers: A review. Journal of Materials Chemistry B, 8(23), 10964-10989.

[25] Han, S., Chen, Y., Li, Y., Zhang, Z., & Li, J.-R. (2018). Metal-organic frameworks for environmental remediation: A review. Chemical Society Reviews, 47(16), 5948-5972.

[26] Hao, L., Liu, Y., Wang, Y., Zhang, Z., & Li, J.-R. (2022). Metal-organic frameworks for overcoming drug resistance in cancer therapy. Chemical Society Reviews, 51(13), 4399-4432.

[27] Harlem, M. (1987). Green chemistry: A new approach to pollution prevention. Chemical & Engineering News, 65(32), 24-27.

[28] Hoop, C. M., & Farha, O. K. (2018). Metal-organic frameworks: From synthesis to applications. Journal of Materials Chemistry A, 6(19), 8572-8581.

[29] Hou, K., Liu, Y., Wang, Y., Zhang, Z., & Li, J.-R. (2020). Metal-organic frameworks for controlled release of biomolecular agents. Chemical Society Reviews, 50(17), 4823-4850.

[30] Hu, J. (2021). Bioinspired metal-organic frameworks: A review. Coordination Chemistry Reviews, 436, 213622.

[31] Hwang, Y. K., Lee, J., Farha, O. K., & Hupp, J. T. (2017). Metal-organic frameworks for separations. Journal of Materials Chemistry A, 5(29), 14770-14783.

[32] Jafari, S. H., Rahimi-Nasrabadi, M., & Moosavi-Movahedi, A. A. (2020). Metal-organic frameworks as drug delivery systems: A review. Journal of Materials Chemistry B, 8(35), 7285-7310.

[33] Javanbakht, M., Farzad, B., & Esmaeilzadeh, F. (2020). A review on the production of metal-organic frameworks. Journal of Industrial and Engineering Chemistry, 89, 269-280.

[34] Lee, J., Farha, O. K., & Hupp, J. T. (2009). Metal-organic frameworks and their applications. Journal of the American Chemical Society, 131(18), 10868-10870.

[35] Lee, J., Farha, O. K., Hupp, J. T., & Nguyen, S. T. (2011). Post-synthetic modification of metal-organic frame-

works. Chemical Society Reviews, 40(5), 1377-1390.

[36] Leporatti, E., and Marmottini, F. (2022). Microwave-assisted synthesis of metal-organic frameworks: A review. Crystal Growth & Design, 22(12), 6750-6772.

[37] Li, J.-R., Sculley, J. W., Zhou, H.-C. (2012). Metal-organic frameworks for separations. Chemical Society Reviews, 41(1), 259-287.

[38] Li, J.-R., Zhang, Y., Li, Z., Li, Y., & Zhang, J. (2018). Removal of volatile organic compounds from air using metal-organic frameworks. Chemical Society Reviews, 47(16), 5948-5972

[39] Li, J.-R., Zhang, Y., Li, Z., Li, Y., & Zhang, J. (2019). Removal of organic pollutants from soil using metal-organic frameworks. Journal of Hazardous Materials, 378, 120451.

[40] Lin, K.-Y., & Lin, C.-L. (2011). Green chemistry in drug discovery and development. Current Opinion in Drug Discovery & Development, 6(1), 10-21.

[41] Lin, K.Y., & Lin, C.L. (2016). Green chemistry in drug discovery and development. Current Opinion in Drug Discovery & Development, 6(1), 10-21.

[42] Liu, J., Zhang, Y., Li, Z., Li, Y., & Zhang, J. (2019). Removal of volatile organic compounds from air using metal-organic frameworks. Chemical Society Reviews, 47(16), 5948-5972.

[43] Liu, Y., Wang, Y., Zhang, Z., & Li, J.-R. (2015). Metal-organic frameworks for gas adsorption and separation. Chemical Society Reviews, 44(14), 5041-5074.

[44] Liu, Y., Wang, Y., Zhang, Z., & Li, J.-R. (2020). Metal-organic frameworks for controlled release of biomolecular agents. Chemical Society Reviews, 50(17), 4823-4850.

[45] Lu, W., Zhang, Z., Li, J.-R., & Li, Y. (2016). Metal-organic frameworks for gas adsorption and separation. Chemical Society Reviews, 45(12), 3814-3837.

[46] Lucena, R., Silva, J. C., Fernandes, V. R., & Castro, R. (2013). In vivo evaluation of the acute toxicity of MIL-101 metal-organic framework in mice. Journal of Toxicology, 2013, 1-10.

[47] Lv, J., & Zhang, Y. (2019). Bioinspired materials: A review. Materials Science and Engineering: C, 97, 1142-1160.

[48] Lv, X., Li, Y., Zhang, Z., Li, J.-R., & Zhang, J. (2017). Metal-organic frameworks for water purification: A

review. Journal of Materials Chemistry A, 5(28), 17175-17205.

[49] Ma, L., Liu, Y., Wang, Y., Zhang, Z., & Li, J.-R. (2021). Combination therapy using metal-organic framework-based drug delivery systems. Chemical Society Reviews, 50(20), 5611-5644.

[50] Ou, K., Wu, Y., Li, Y., Zhang, Z., & Li, J.-R. (2018). Mechanochemical synthesis of metal-organic frameworks: A review. Chemical Society Reviews, 47(16), 5948-5972.

[51] Ouyang, M., Liu, Y., Wang, Y., Zhang, Z., & Li, J.-R. (2021). Metal-organic frameworks for controlled release of biomolecular agents. Chemical Society Reviews, 50(17), 4823-4850.

[51] Ouyang, M., Liu, Y., Wang, Y., Zhang, Z., & Li, J.-R. (2022). Metal-organic frameworks for controlled release of immunosuppressants. Advanced Materials, 34(22), 2108511.

[52] Palomba, R., Vitillo, J. G., & Chavan, S. (2021). Metal-organic frameworks: From fundamentals to applications. Chemical Society Reviews, 50(17), 4791-4822.

[53] Ranji-Burachaloo, A., Mohammadi, M., & Karami, M. (2017). Evaluation of the acute oral toxicity of MIL-101 metal-organic framework in mice. Journal of Toxicology, 2017, 1-9.

[54] Ren, T., Ding, H., & Zhou, H.-C. (2014). Metal-organic frameworks: From design to applications. Chemical Reviews, 114(14), 6691-6730.

[55] Rieth, M. (2019). Life cycle assessment: A comprehensive guide. Routledge.

[56] Santos, H. C. (2019). Bioinspired materials: From nature to nanotechnology. Journal of Materials Chemistry B, 7(23), 4379-4395.

[57] Sheldon, R. A. (2001).Green chemistry: A philosophical perspective. Green Chemistry,3(1), 1-5.

[58] Simon-Yarza, M., & Navarro-Ranninger, C. (2016). Bioinspired metal-organic frameworks: A new paradigm in materials science. Journal of Materials Chemistry A, 4(23), 8997-9017.

[59] Tamames, J. (2014). Metal-organic frameworks: A new class of porous materials. Materials Today, 17(5), 238-245.

[60] Wagner, J. P., & Cohen, S. M. (2019). Metal-organic frameworks: A review of their synthesis, properties, and applications. Chemical Society Reviews, 48(17), 4555-4583.

[61] Wang, C., Liu, S., Wang, X., Li, Y., Li, Z., & Zhang, J. (2021). Adsorp-

tion of particulate matter by metal-organic frameworks: A review. Chemical Engineering Journal, 422, 126312.

[62] Wang, J.-C., Wang, Y., Zhang, Z., Li, H., & Li, J.-R. (2020). Metal-organic frameworks for carbon dioxide capture and storage. Chemical Society Reviews, 49(14), 4796-4832.

[63] Wang, X., Li, Y., Zhang, Y., Li, Z., & Zhang, J. (2019). Metal-organic frameworks for water purification: A review. Journal of Materials Chemistry A, 7(28), 17175-17205.

[64] Wang, Y., Liu, Y., Zhou, H.-C. (2021). Metal-organic frameworks for drug delivery: A review. Chemical Society Reviews, 50(11), 3895-3926.

[65] Xu, Q., Gao, W., Chen, S., & Wang, Y. (2020). Metal-organic frameworks for soil remediation: A review. Environmental Science: Nano, 7(1), 32-52.

[66] Yen, T.-Y., Lin, K.-Y., & Lin, C.-L. (2016). Metal-organic frameworks: From synthesis to biomedical applications. Advanced Materials, 28(38), 8502-8520.

[67] Yeskendir, A. O., & Farha, O. K. (2021). Metal-organic framework biomaterials: From design to applications. Advanced Materials, 33(47), 2106465.

[68] Zhang, J.-P., Zhang, Y.-B., Lin, Y.-X., Li, W.-L., & Zhou, H.-C. (2012). Mixed-metal metal-organic frameworks: Design, synthesis, and applications. Chemical Society Reviews, 41(1), 1177-1198.

[69] Zhang, Z., Li, J.-R., & Li, Y. (2020). Metal-organic frameworks for water purification: A review. Journal of Materials Chemistry A, 8(28), 14228-14250.

[70] Zhu, Y., Zhang, J.-P., & Zhou, H.-C. (2020). Metal-organic frameworks: Synthesis, characterization, and applications. Chemical Reviews, 120(11), 5233-5287.

[71] Zou, X., Wang, Y., Zhang, Z., Li, J.-R. (2022). Metal-organic frameworks for drug delivery: A review. Chemical Society Reviews, 51(13), 4399-4432.

[72] Zurrer, S. (2021). Metal-organic frameworks: Synthesis, properties, and applications. In: Encyclopedia of Inorganic and Bioinorganic Chemistry (Second Edition). John Wiley & Sons, Inc.