# Research on Heavy Metal Ion Adsorption Using Metal Organic Frameworks (MOFs) Materials

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Abstract: Heavy metal contamination has led to significant environmental issues and poses risks to human health. Among various methods for treating heavy metals, adsorption is particularly effective. Metal-organic frameworks (MOFs), as a highly promising new class of adsorbents, excel in addressing complex heavy metal pollution due to their superior adsorption capabilities. This paper aims to analyze the sources and hazards of heavy metal pollution and to investigate the advantages of MOFs in the adsorption of heavy metals. In this paper, it is concluded that MOFs materials are mainly categorized into six series such as ZIF and UiO. Numerous MOFs have demonstrated remarkable adsorption efficiency for common heavy metals such as lead, mercury, chromium, and arsenic. However, there are still challenges in the practical application of MOFs materials such as enhancing the stability of the materials in the actual water body; making the materials take into account a variety of excellent properties; and discovering cost-effective methods to prepare MOFs materials. This paper can provide a feasible reference for heavy metal treatment.

## 1 INTRODUCTION

In recent years, increased industrial activity, especially in sectors like metallurgy and battery production, has released large amounts of heavy metals, including mercury and lead, severely impacting the environment. Smelting operations alone contribute approximately 40-73% of human-generated heavy metal emissions. Most heavy metals are not biodegradable and are easily transferred and enriched among organisms, eventually entering the human body through the food chain (Zhang, 2022). Excessive concentrations of heavy metals can cause serious harm to the human respiratory and digestive systems and may even be life-threatening. Therefore, it is imperative to control heavy metal pollution.

Chemical precipitation, membrane filtration, and ion exchange have been used to treat heavy metal wastewater, but most of the methods are costly and complicated to operate in the application process and may cause secondary pollution. In recent years, adsorption has become a powerful heavy metal treatment method and has been widely used for the efficient removal of heavy metals from water (Lin, 2023). Therefore, it has become a trend to prepare new adsorbents that combine high adsorption performance with green and non-polluting properties. In recent decades, metal-organic frameworks (MOFs), as new organic-inorganic hybrid materials, have attracted much attention due to their ordered porosity, large specific surface area, well-proportioned structural cavities, and thermal and chemical stability. Moreover, these properties have been demonstrated in studies of the ZIF, MIL, and UiO series. This means that organic ligands and various metals can be combined as expected (Ru, 2021). The properties of MOF can effectively promote the adsorption of targets on the MOFs surface. MOFs materials are more advantageous than conventional adsorbents in heavy metal adsorption.

The purpose of this paper is to introduce the application performance and potential of various MOFs materials in heavy metal ion adsorption and to predict and prospect the application prospect of MOFs materials. This paper will discuss the sources and hazards of heavy metals, the definition and classification of MOFs materials, and the adsorption performance of MOFs materials on heavy metals, and analyze the application of MOF materials in heavy metal adsorption.

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# 2 SOURCES AND HAZARDS OF HEAVY METAL IONS

In terms of environmental pollution, heavy metals are chromium, mercury, lead, arsenic, and other biotoxic heavy metals and metalloids. The five most toxic to humans are arsenic, chromium, lead, mercury and cadmium. Industrial pollution is the main source of heavy metals, most of which are discharged into the environment through industrial wastewater and waste residues, and subsequently enriched in the human body, animals, and plants, thus jeopardizing the environment and human health. Heavy metal pollution is mainly reflected in water pollution but also exists in the atmosphere and solid waste. Unlike organic pollutants, heavy metals are difficult to degrade through physical, chemical, or biological processes in nature and are easily enriched in the environment and living organisms. Heavy metals cannot be broken down when they enter a body of water and can combine with other toxins in the water to form more toxic substances (Lei, 2023). They interact firmly with enzymes and proteins in the body, which leads to the inactivation of biomolecules, resulting in chronic or acute poisoning that poses a serious threat to human health.

# 3 DEFINITION AND CLASSIFICATION OF MOFS

The treatment of heavy metal pollution is urgent. MOFs, as new adsorbents in the adsorption method, have great potential in heavy metal adsorption. This paper will center on four types of MOFs to understand their characteristics and differences.

MOFs are crystalline porous materials formed by linking inorganic metal nodes with organic ligands, creating a periodic network structure (Chen, 2023). In general, MOFs consist of two components, the organic ligand and the metal center, which play the roles of pillars and nodes, respectively (Kaur, 2023). Representative classical MOF materials are IRMOFs, ZIFs, MIL, and UiO series.

Isoreticular MOFs (IRMOFs) series of materials are formed by the coordination of Zn2+ with the oxygen in the terephthalic acid root, and the pore sizes and porosities of the materials are different depending on the length of the organic ligands and the substituents on the benzene rings of the ligands (Eddaoudi, 2002). However, because of the similar synthesis methods, the materials have the same topology and are thermally and chemically stable.

Zeolitic Imidazolate Frameworks (ZIFs) are constituted by the coordination of metal ions with tetrahedral coordination ability, such as Zn2+ and Co2+, with nitrogen atoms in the imidazole moiety (Cravillon, 2009). Because of the topological similarity to zeolite, the ZIFs series are also known as zeolite imidazolium ester backbone materials. The ZIFs series are well-stabilized with good thermal (up to 550° C), aqueous, and solution stability (alkaline solutions, organic reagents), and can be used for contaminant removal from water.

Material Institute Lavoisier (MIL) series materials are constituted by coordination of metal ions such as Fe3+, Cr3+, and Al3+with oxygen in dicarboxylic acid ligands, and generally have good solvent and thermal stability (Horcajada, 2010). The skeletons of these materials are flexible and can undergo large reversible deformation under external stimuli.

The University of Oslo (UiO) series of isostructured MOFs, composed of Zr4+ ions bonded to organic ligands, exhibit high stability (Cavka, 2008). UiO-66, the most representative structure, features Zr6O4(OH)4 as the secondary building unit. This unit consists of a Zr6 octahedral core coordinated with 12 terephthalic acid ligands, resulting in a highly symmetric structure. The strong interaction between the Zr6 core and the carboxyl groups of the ligands contributes to the excellent water and thermal stability of the Zr6 octahedron.

The above four MOFs materials and their derivatives have already shown excellent performance in heavy metal adsorption treatment, proving the potential of MOFs materials.

# 4 ADSORPTION PROPERTIES OF MOFS ON HEAVY METAL IONS

## 4.1 Plumbum (Pb)

Pb is a polluting heavy metal with a relative atomic mass of 207. 2. Pb has a significant effect on human health, and the damage to the bone marrow hematopoietic system and the nervous system is very serious. Roy et al. constructed ZIF-8 and used it for adsorption of Pb(II) by solvent-thermal method (Roy, 2021), and the results of their study show that the adsorption of Pb(II) by ZIF-8 is best when the solution is weakly acid to neutral; in alkaline environment Pb(II) mainly remains in the form of precipitation and gel such as Pb(OH)2, at this time the adsorption turns to physical adsorption.

The carboxylation modification can lower the isoelectric point of the MOFs, thus allowing them to adsorb Pb(II) efficiently even at lower pH. Zhao et al. constructed UiO-66-(COOH)2 using homophthalic acid, which is a MOFs with extreme acid-resistant stability, and which maintains an adsorption capacity of more than 200 mg/g of Pb(II), even at a pH of 2 (Zhao, 2019). The carboxylation modification also enhanced the recycling performance of UiO-66-(COOH)2, which could still recover about 85% of its adsorption performance after four adsorption-desorption cycles. At lower pH, Pb(II) mainly remains in the form of hydrated ions with larger particle sizes. In order to further enhance the adsorption performance of MOFs for Pb(II) at lower pH, Li et al. used tartaric acid to post-synthesize the modification of UiO-66-NH2, and the results showed that the exchange of tartaric acid for 2-amino terephthalic acid disrupted the microporous framework of UiO-66-NH2, and on the MOFs mesopores ranging from 26 to 50 nm and macropores ranging from 50 to 120 nm appeared, and the oversized pore structure not only promoted the diffusion of Pb(II) inside the MOFs, but also elevated the rigidity of the MOFs, which exhibited the maximum saturation adsorption of Pb(II) at 186. 14 mg/g (Li, 2020).

## 4.2 Mercury (Hg)

Hg belongs to the typical heavy metal atoms with a relative atomic mass of 200. 6. Hg readily binds to proteins and enzymes, inhibiting their biological activities and possibly inactivating them. Hasankola et al. constructed carboxylate-rich Zr-TCPP using 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin and Zr(IV) (Hasankola, 2020). The results show that when the pH is low, the adsorption of Hg(II) on Zr-TCPP mainly relies on cation-π electron cloud interactions and ion exchange, and the interactions are gradually transformed into electrostatic interactions and ligand interactions with the increase of pH, and the adsorption is transformed into the deposition and filling of Hg(OH)2 in the pores of Zr-TCPP when the pH exceeds the precipitation value of Hg(II)

Altering the porous nature of MOFs is beneficial in enhancing the interaction with Hg(II). Alshorifi et al. introduced Co(II) with different coordination numbers during the construction of MIL-101(Fe). The porosity and specific surface area of MOFs reached the maximum when the molar ratio of Co(II) to Fe(III) was 1:1. At this time, the carboxyl group exposed in MOFs was also the highest, and the Hg(II) adsorption up to 312. 97 mg/g (Alshorifi, 2022). Ji et al. prepared MOF-808-SH by post-synthetic modification via ligand-exchange method using α-mercaptoacetic acid to exchange formic acid in the structure of MOF-808. The reactive carboxyl groups on the MOF-808-SH could sequester Hg2+ at lower pH, while the sulfhydryl group could to form stable uncharged complexes with Hg(OH)+ and Hg(OH)2 at higher pH (Ji, 2022).

## 4.3 Chromium (Cr)

Cr is one of the essential micronutrients for plants and animals, with a relative atomic mass of 52. 01, but excess Cr has a strong biotoxicity, in which Cr(VI) is about one hundred times more toxic than Cr(III). The distribution pattern of Cr(VI) in the water body is related to the pH and concentration, and Noraee et al. found that UiO-66 has a stronger adsorption capacity for low concentrations of $HCrO^{4-}$ under weakly acidic conditions, when UiO-66 showed a stronger positive charge (Noraee, 2019). Since UiO-66 has denser pores, $HCrO^{4-}$ is converted to $H_2CrO_4$ when the pH is about 2, when the physical adsorption of $H_2CrO_4$ on the appearance of MOFs mainly occurs. To enhance the adsorption performance of Cr(VI) at low pH, Rego et al. constructed a Ce(III)-doped UiO-66, and the difference in the coordination number caused a certain amount of mesopores to appear in the microporous structure of UiO-66, and the generation of mesoporous structure with larger pore size allowed $H_2CrO_4$ to be still deposited in the pore space of Ce-UiO-66 in acidic conditions, which showed an excellent adsorption capacity for Cr(VI)(Rego, 2021).

## 4.4 Arsenic (As)

As belongs to the class of heavy metals, has the nature of amphoteric elements, the relative atomic mass is 74. 92, As will inhibit the biological activity of enzymes and cause metabolic hindrance. The existence of As in the water body is mainly in the form of As(III) and As(V). The morphology of As(III) is related to pH, and the As(III) mainly remains in the form of $H_3AsO_3$ when the pH is less than 9. 1. Pervez et al. found that under weakly alkaline conditions $H_3AsO_3$ is more easily exchanged with MOF-808 in ligands, and its adsorption performance is enhanced with the increase of surface carboxyl group content; at pH greater than 9. 1, the As(III) mainly remains in the form of $H_3AsO_3$. Alkaline conditions $H_3AsO_3$ is more susceptible to ligand exchange with MOF-808, and its adsorption performance is enhanced with the elevation of the carboxyl group content on the surface;

at pH greater than 9. 1, As(III) then exists in the form of $H_3AsO^{2-}$, which can be adsorbed onto MOFs through electrostatic interactions and interactions between anionic-π electron clouds, but there is a high requirement for alkali resistance of MOFs (Pervez, 2022). Highly oxidizing functional groups or metal ions can also be present in MOFs, e.g., MOFs containing Mn(IV) can oxidize the more reducing As(III) to As(V) under acidic conditions, but this redox reaction causes irreversible defects in the framework of MOFs.

Amination modification can enhance the positive electronegativity of MOFs, thus enhancing their adsorption performance for As(V). Yin et al. showed that MIL-101(Fe/Al)-NH2 could adsorb more than 90% of As(V) efficiently in the pH range of 3-11. Under acidic conditions, this adsorption is mainly dependent on the electrostatic interaction of protonated amino groups with As(V) (Yin, 2022). If the MOFs are simultaneously modified by carboxylation and amination, the carboxyl and amino groups can also form a stable hydrogen-bonding network and synergistically adsorb As(V), which effectively weakens the conformational distortion of the organic ligand, enhance the rigidity of the MOFs, and improve the water stability of the MOFs.

## 5 CHALLENGE

Among the many properties of MOFs, porousness, surface activity, and framework flexibility are the core properties of MOFs as adsorbents. The water stability, scalability, biotoxicity, and recyclability of MOFs are the key to their use as adsorbents in high-performance water treatment fields. A breakthrough in certain properties of MOFs can be realized by modulating metal ions, organic ligands, and synthesis methods. Although some progress has been made in the preparation methods, performance studies, and multidimensional applications of MOFs in recent years, the practical application of MOFs for the adsorptive removal of heavy metal ions still faces many challenges.

(1) Although MOFs show some stability in neutral, acidic, and alkaline solutions, in the actual water body, which contains more strongly liganded organic matter and metal ions, this ligand or metal ion exchange can destroy the structure of MOFs. Meanwhile, in order to increase the adsorption capacity of MOFs, the synthesis conditions or functionalization modification are usually changed to expose more active functional groups, but such MOFs with higher adsorption capacity often have more obvious structural defects, and MOFs with structural defects often imply the loss of water stability and recyclability, so there is still a need for in-depth study of the equilibrium between the adsorption performance and the water stability of MOFs.

(2) Although MOFs possess excellent porosity, framework flexibility, scalability, surface activity, water stability, recyclability, and low biotoxicity, it is difficult for MOFs applied to water treatment to have almost all of the above properties at the same time, such as scalability and surface activity, water stability and surface activity, framework flexibility and water stability, framework flexibility and recyclability, and biotoxicity and porosity. It is difficult to have all of these properties at the same time, so how to balance the bond between the various advantages of MOFs and prepare high-performance adsorbents for water treatment still needs to be further researched.

(3) Currently, MOFs applied to heavy metal adsorption are mostly tiny powder particles, and the adsorption of heavy metal ions is still at the stage of laboratory exploration, and the studies on the biotoxicity and scalability of MOFs are still immature, so it is still necessary to analyze the mechanism of their environmental effects such as migration, cycling, and enrichment in ecological environments, as well as the preparation of wholesale MOFs with low-cost and high efficiency.

## 6 CONCLUSION

This paper discusses the sources and hazards of heavy metal pollution, the definition and classification of MOFs, with the adsorption of heavy metals by MOFs as the main line. Heavy metals refer to metals and metalloids that are significantly biotoxic and originate from industrial pollution, transportation pollution and domestic waste pollution. In nature heavy metals are difficult to degrade by physical, chemical or biological processes and are easily enriched in the environment and in living organisms. Heavy metals entering water bodies may combine with other toxins in the water to form more toxic substances, which can interact strongly with enzymes and proteins in the human body and pose a serious threat to human health. The definition and classification section of MOFs introduces four representative classes of classical MOFs materials, namely, IRMOFs, ZIFs, MIL, and UiO. From the perspective of the adsorption of four major heavy metals, namely, Pb, Hg, Cr, and As, by MOF materials and their derivatives, the adsorption performances and related adsorption mechanisms that have been reported to have been demonstrated by MOFs and their derivatives materials in the application of treatment of these four heavy metal pollutions are discussed. The future development of MOF materials in the field of heavy metal adsorption is still challenging in terms of the improvement of adsorption performance and actual water stability, the balance between various excellent properties, and the balance between cost and benefit. The aim of this paper is to provide referable solutions for the application of MOFs in the field of heavy metal adsorption.

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