Application of Metal-Organic Frameworks for the Adsorptive Extraction of Heavy Metals from Contaminated Water

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Abstract. The water pollution caused by heavy metals has become a significant environmental issue in modern cities. Metal-organic frameworks (MOFs) have demonstrated outstanding potential as advanced adsorbents for the selective removal of heavy metals from aqueous systems. The utilization of MOFs characterized by their unique structures and properties, for the adsorption of heavy metals from wastewater has garnered significant attention from researchers. This capability is primarily from their adjustable structural configurations and unique surface chemical properties. By considering toxic metals such as Hg (II), Pb (II), As (III/V), and Cr (VI), this paper explores targeted structural design strategies based on the characteristics of MOFs to achieve efficient and selective capture. The research analyzes the adsorption mechanisms from both physical and chemical perspectives, including π-π interaction, electrostatic interactions, and functional group-specific recognition. Additionally, this paper also deeply discusses the optimization of performance parameters, engineering implementation paths, and comprehensive analysis of the environmental and biological hazards, while elaborating on the advantages and mechanisms of heavy metal adsorption by MOFs materials, also some key challenges like structural stability and scalability faced by MOFs in real-world applications.

1 Introduction

The pollution of water bodies by heavy metals has already sparked among the most severe environmental problems worldwide. Heavy metals such as chromium, mercury, lead, cadmium, and arsenic are extremely difficult to decompose by microorganisms [1]. Instead, they tend to accumulate more easily in aquatic sediments and various living organisms. Due to their complex composition characteristics, the treatment of these pollutants becomes particularly challenging. For example, for lead ions (Pb^{2+}), even at low levels of exposure, they can cause irreversible neurological and cognitive damage to children. Hexavalent chromium (Cr (VI)) is classified as a harmful carcinogen to the human body. It has a very close correlation with cancers in the lungs and nasal sinuses, mainly because it has high mobility and the ability to trigger oxidative stress reactions in biological systems. Arsenic exists mainly in the form of arsenite or arsenate, and its toxicity is extremely strong.

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Longterm exposure to arsenic is likely to cause skin lesions, cardiovascular system disorders, and various types of cancers [2]. Therefore, it is urgent to develop efficient remediation technologies. This is an important task that must be fully accomplished to ensure water body safety and public health.

Traditional adsorption technologies, such as activated carbon and zeolites, have been widely used in water treatment. However, they have some obvious drawbacks, such as low selectivity when dealing with specific heavy metal ions and certain limitations in their adsorption capacity. These shortcomings make it difficult to achieve precise separation and efficient removal of target pollutants in complex water bodies. Metal-organic frameworks (MOFs), a new type of porous crystalline material, demonstrate great potential in the selective adsorption of heavy metals due to their adjustable pore structures and modifiable surface chemical properties. Given the significant potential of MOFs in this field and the existing.

2 Design strategies of MOFs for specific heavy metals

To achieve efficient and selective removal of various heavy metal ions, targeted functionalization strategies have been developed based on the chemical species and soft-hard acid-base properties of the contaminants.

For Hg (II), Pb (II), and As (III), these kinds of metal ions are classified as soft acids and show a stronger affinity for soft-base ligands.

Due to low cost and superior performance, Cu is widely used in the synthesis of MOFs.

Copper metal-organic framework materials (Cu-MOFs) are a type of metal-organic framework material with a high specific surface area. Chui first reported the synthesis of Cu-MOFs in 1999, $[Cu_3 (TMA)_2 (H_2 O)_3]n$. It has good structural stability, high thermal stability, and high experimental reproducibility. It can selectively adsorb and separate some pollutants to achieve excellent results [3, 4].

Highly oxygen-affinity metals such as Zr have also been proven to be another approach for obtaining more stable MOFs. Zirconium-based MOF materials are MOF materials synthesized with zirconium as the metal core. They overcome the shortcomings of traditional MOF materials, such as instability in aqueous solutions and easy collapse of the framework, and possess excellent hydrothermal stability. The UiO series is a type of MOF material based on zirconium metal, and UiO-66 is the most typical. In 2008, Cavka first reported the synthesis of UiO-66. The removal rates of Cu (II), Cd (II), Pb (II), and Hg (II) in the wastewater can reach 99.45%, and the effective column volume for treating Hg (II) is as high as 840BV. Jiang utilized click chemical reactions and Zr-MOFs materials to react the azide groups present on the organic ligands in the materials with olefin-containing compounds, thereby obtaining different functionalized groups. Moreover, by altering the content of azide groups in the framework, they were able to achieve the quantitative synthesis of new functionalized groups [5-7].

Furthermore, aluminum-based MOFs can effectively remove heavy metal ions from water. In 2014, Guoli synthesized NH_2-MIL-101 (Al) using the hydrothermal solvent method and applied it to remove heavy metal pollutants, arsenic from water. The results show that NH_2-MIL-101 (AI) has a good removal effect on heavy metal arsenic, with an adsorption capacity of up to 85.2 mg/g. Moreover, by using the post-modification synthesis method, different amounts of ethylenediamine were grafted onto MIL-101 to modify it. The amino groups were introduced into the pore structure of MIL-101, and amino-functionalized MIL-101 was synthesized. Research shows that not only has the adsorption capacity significantly increased, but it also exhibits excellent performance in multiple aspects [3, 8].

Iron-based MOFs possess advantages such as large pores, large specific surface area (provides a large number of physical adsorption sites), and easily modifiable pore surfaces.

Due to the ease of modification of their pore surfaces, they can exhibit the ability to selectively adsorb certain guest molecules with specific functional groups. Thanh synthesized Cr-MIL-101 and Fe-MIL-101 and compared their performance in adsorbing Pb^{2+} . The results showed that the maximum single-layer adsorption capacity of Fe-MIL-101 was 86.20 mg/g, which was much higher than that of Cr-MIL-101 (57.96 mg/g) [9, 10].

The target adsorbed metals by MIL-101 (Fe) are Sb (III) and Sb (V), with the maximum adsorption capacities reaching 151.81 and 472.83 mg/g, respectively. Within two hours, 98.1% of Sb (V) can be removed, indicating that MIL-101 (Fe) exhibits excellent adsorption for both valence states of antimony, and is particularly efficient for Sb (V) [3, 10-12].

3 The interaction mechanisms of heavy metal adsorption on MOFs

The adsorption process in MOFs for heavy metal removal is usually driven by the combined effects of several forces. There exist various complex interactions, such as electrostatic interaction, aromatic cycle π–π stacking interaction, and hydrogen bonding, between the external surfaces of MOFs and dye molecules.

3.1 Analysis of the key attractive forces in adsorption

Metal-organic frameworks (MOFs) possess high specific surface area, controllable pore structure, and diverse surface functional groups, which make them highly promising in the field of organic pollutant adsorption.

3.1.1 Physical adsorption

Physical adsorption is an adsorption process caused by intermolecular forces (such as Van Der Waals forces, electrostatic forces) [13]. It is one of the main mechanisms for MOFs to adsorb organic pollutants. The high specific surface area and controllable pore size of MOFs provide a large number of adsorption sites, which are conducive to the diffusion and adsorption of organic pollutants. For instance, heavy metal ions tend to form stable bonds with either unsaturated metal sites on the MOF structure or functional groups attached to the porous framework. This specific binding not only supports the good selectivity of MOFs for target heavy metals but also provides the basis for their high adsorption capacity trait. Electrostatic interactions are also very important for capturing charged pollutants. Pore sieving and size exclusion, a special advantage of MOFs thanks to their precisely adjustable pore sizes, let metal ions of matching sizes enter and get trapped while keeping out larger molecules or hydrated ion clusters, which further improves the adsorption selectivity. Electrostatic interactions are also crucial for capturing charged pollutants. And through the precisely adjustable pore size of MOFs, pore channel sieving and size exclusion can play roles: metal ions with matching sizes can enter and be captured, while larger molecules or hydrated ion clusters are blocked out, thereby further enhancing the selectivity of adsorption MIL-101 (Fe) adsorbs Pb^{2+} . The Pb^{2+} ions interact with the negatively charged MOF framework surface through electrostatic forces [10, 14].

3.1.2 Chemical adsorption

Chemical adsorption refers to the formation of stable chemical bonds between the adsorbent and the adsorbed substance, usually involving coordination bonds, hydrogen bonds, or covalent bonds. MOFs have abundant surface functional groups, such as carboxyl groups, amino groups, and hydroxyl groups, which can form chemical bonds with the functional groups on organic pollutants, thereby enhancing the adsorption capacity. The adsorption capacity of MIL-101 (Fe) for Sb (V) is as high as 472.83 mg/g, which is also based on the Fe–O–Sb coordination interaction [11].

3.1.3 π-π interaction

Besides these main forces, secondary interactions like π-π interactions often act as an extra stabilizing factor, helping to strengthen the adsorption structure and make the binding more stable. For organic pollutants with aromatic ring structures, specific ligands in MOFs (such as benzoic acid or p-benzoic acid) can form π-π interactions with the aromatic rings of the organic pollutants, thereby enhancing the adsorption capacity. The maximum adsorption capacities of UiO-66 for methyl red (MR), methyl orange (MO), malachite green (MG), and methylene blue (MB) dyes are 384, 454, 133, and 370 mg/g, respectively, enabling efficient adsorption of the dyes [13].

3.2 The factors influencing the adsorption mechanism of MOFs

The adsorption efficiency of MOFs for heavy metal ions is a complex process determined by the material's own structure, the characteristics of the target ions, and the external environmental conditions.

Firstly, the intrinsic properties of MOFs are the basis for adsorption, their pore structure (pore size and distribution) determines the accessibility and diffusion path of ions; high specific surface area provides abundant adsorption sites; and the types and density of surface functional groups (such as carboxyl, amino groups) directly determine the chemical selectivity and coordination mechanism for specific heavy metals.

Moreover, the properties of the heavy metal ions themselves - including charge level, ion radius size, and hydration energy strength - profoundly affect their affinity with the active sites of MOFs, the resistance to migration in the pores, and the ease of dehydration complexation.

Finally, the solution environment (especially the pH value) is a key variable for achieving dynamic regulation: it significantly affects the selectivity and capacity of adsorption by altering the surface charge state of the metal-organic framework materials and the forms of heavy metal ions (such as hydrolysis or complexation); [11] ionic strength can both shield electrostatic interactions and potentially spark competitive adsorption， and temperature simultaneously both influences the kinetics and thermodynamic equilibrium of adsorption. These three factors are not independent but are coupled and mutually restrictive. Only by rationally designing MOF materials and precisely matching the characteristics of target ions to optimize operating conditions can efficient, highly selective, and stable heavy metal adsorption removal be achieved.

4 Performance optimization and engineering considerations

4.1 Critical performance evaluation

Adsorption kinetics is usually modelled using first-order or second-order kinetic equations, which determine the contact time required for water treatment processes. Therefore, it is of crucial importance for the design of actual treatment systems. In wastewater matrices with complex compositions, the target heavy metal ions often coexist with a large number of competing ions, such as calcium ions and sodium ions. At this time, the high selectivity of the adsorbent towards the target pollutants is indispensable. This performance indicator is usually determined through competitive adsorption experiments and calculated using the selectivity coefficient [6].

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1 \cdot (q_e - q_t) \tag{1}$$

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2 \cdot (q_e - q_t)^2 \tag{2}$$

Equation (1) and (2) above is first-order kinetic model and second-order kinetic model.

4.2 Engineering strategies for enhanced applicability practical

Regarding the core issue of the hydrolysis stability of metal-organic frameworks (MOFs), currently, two main solution strategies are adopted: the first is to utilize MOFs materials with stable structures - among which zirconium-based MOFs (such as the UiO series) and some iron-based metal-organic framework materials (MIL series) are the most typical; the second is to prepare MOFs composite materials. In these composite materials, MOFs particles will be encapsulated or loaded onto matrix materials such as chitosan, alginate, porous silica, or activated carbon [3]. This design not only enhances the mechanical strength of the material but also reduces the risk of structural disintegration in the water environment.

5 Challenges and future perspectives

In order for metal-organic framework (MOF) materials to be used in water treatment applications, many key issues still need to be addressed. Corresponding research directions have appeared to overcome these obstacles. Firstly, the stability of MOFs in water environments is particularly crucial and needs to be resolved as soon as possible: fluctuations in pH, changes in ionic strength, and the presence of organic solvents can all affect their crystal structure, therefore weakening their adsorption performance and shortening the MOFs' lifespan. To solve this problem, researchers are developing more stable alternative materials, optimizing the synthesis process of MOFs, and incorporating automation technology, which is essential for addressing issues related to low production efficiency and quality control in large-scale production, in order to achieve the large-scale preparation of high-quality materials.

In order to achieve efficient and economical results in water treatment, it is necessary to comprehensively enhance the adsorption capacity and selectivity of metal-organic framework materials (MOFs) for precise pollutants. This can be achieved through surface functionalization modification, regulation of pore structure, which enables accurate adjustment of the surface properties and pore microenvironment of the materials. In practical applications, the regeneration and recycling of MOFs are key stages for reducing the operation costs and ensuring the sustainability of the technology.

6 Conclusion

Metal-organic frameworks (MOFs), with their controllable structures and adjustable functions, exhibit application potential in the field of removal of heavy metal-contaminated wastewater treatment. Researchers can modify the surface of MOF materials according to the physical and chemical properties (such as pH value) and ionic forms of target heavy metals, therefore to prepare advanced adsorbents with high selectivity and high adsorption capacity.

These materials can accurately capture specific pollutants from different and complex aqueous systems, which effectively overcomes the traditional water treatment technologies.

Although there are still many challenges that need to be addressed - including high production costs for large-scale production, insufficient long-term stability in harsh water environments, and environmental management issues throughout the life cycle of MOFs materials - these problems also provide clear directions for future research. With continuous innovation at the material level and in-depth research on engineering technology, MOFs will become the core component of the next generation of water treatment systems. Their irreplaceable application prospects will provide solid technical support for promoting the development of global water security.

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