Research on the Efficient Removal and Recycling of Heavy Metals Based on MOFs-Derived Nanomaterial

Hongwei Zhang

School of Material Engineering,Hebei University of Science and Technology

1151807134@qq.com

Abstract. Heavy metal pollution seriously threatens the ecological environment and human health. Due to their unique structural characteristics, metal-organic framework materials (MOFs) and their derived nanomaterials have shown great potential in heavy metal pollution control. This article comprehensively reviews the research progress of these materials in removing and recycling heavy metals, covering preparation methods, the mechanism of action, application examples, and challenges and prospects. It focuses on the impact of different preparation conditions on the structure and performance of the materials, deeply analyzes the interaction mechanism between the materials and heavy metals, lists practical application cases and analyzes their advantages and limitations, aiming to provide a reference for the development of more efficient, economical, and environmentally friendly heavy metal pollution control technologies.

Keywords: Metal-organic frameworks; MOFs-derived nanomaterials; Heavy metal removal; Recycling; Mechanism of action.

1. Introduction

Industrial activities such as electroplating, mining, and electronics manufacturing discharge large amounts of wastewater contaminated with toxic heavy metals (e.g., Pb^{2+}, Hg^{2+}, Cr(VI), As(III)). These non-biodegradable ions accumulate in the food chain, causing serious health risks including cancer and neurological damage [1–2]. Over 5 million tons of heavy metals are released globally annually, with about 30% contaminating water and soil [2]. Conventional treatment methods—such as activated carbon adsorption, chemical precipitation, and ion exchange—suffer from low capacity, poor selectivity, sludge generation, and sensitivity to high salinity [3–6].

Metal–organic frameworks (MOFs) are porous materials formed by metal ions and organic ligands, offering ultra-high surface areas and tunable pores [7]. However, their application is limited by poor water stability and mechanical strength [8]. Through pyrolysis, carbonization, or hydrothermal treatment, MOFs can be converted into derived nanomaterials (e.g., metal oxide/carbon composites, N-doped porous carbons) that retain porosity while gaining enhanced stability and adaptability [9]. These materials exhibit high adsorption capacity (e.g., 520 mg/g for Pb^{2+} [10]), function across a broad pH range (3–11) and high salinity (<15%) [11], and maintain over 80% capacity after 10 regeneration cycles [12].

This review consolidates recent progress in MOF-derived nanomaterials for heavy metal removal and recycling, addressing synthesis, mechanisms, applications, and challenges. It aims to bridge laboratory research and industrial implementation by evaluating cost, scalability, and real-world performance.

2. Heavy Metal Removal Mechanisms of MOF-Derived Nanomaterials

2.1 Adsorption Mechanism

Adsorption is the most common mechanism for heavy metal removal by MOF-derived nanomaterials, which can be divided into physical and chemical adsorption. The two mechanisms usually coincide, and chemical adsorption plays a dominant role in determining the adsorption capacity and stability of the material.

Physical adsorption relies on van der Waals forces, electrostatic interactions, and pore filling. For example, N-doped carbon from ZIF-67 uses mesopores (2–8 nm) to adsorb Pb^{2+}, contributing 30% of total capacity, while protonated $-NH_3^+$ sites attract CrO_4^{2-} electrostatically in acidic conditions [13]. Microporous carbon from MOF-5 selectively adsorbs hydrated Cd^{2+} (selectivity coefficient = 28) via size exclusion [14]. However, physical adsorption is sensitive to pH and ionic strength.

Chemical adsorption involves stronger interactions such as coordination or covalent bonding. Surface -OH groups on α-Fe_2O_3 form bidentate complexes with As(III) (adsorption constant: 1.2×10^5 L/mol [15]), while $-NH_2$ groups coordinate with Hg^{2+} even in 10% NaCl [16]. Thiol groups form stable Hg–S bonds (bond energy: 270 kJ/mol), enabling 99% Hg^{2+} removal in mixed solutions [17]. Precipitation also occurs, e.g., Fe_3O_4 reacting with As(V) to form $FeAsO_4$ [18]. Modifying surface functional groups can enhance chemical adsorption.

2.2 Reduction Mechanism

Reductive components (e.g., zero-valent metals or pyridinic N) convert toxic high-valence metals to less toxic low-valence states. ZIF-8-derived Zn^0/NC reduces Cr(VI) to Cr(III), which is then chelated by surface -OH; total capacity reaches 420 mg/g [19]. Fe^0 in MIL-88A-derived materials oxidizes As(III) to As(V), with a 98.5% removal rate [20]. Pyridinic N in ZIF-67-derived carbon reduces Hg(II) to Hg(0), achieving 99.2% removal [21]. Reduction efficiency depends on the content and type of reductive sites.

2.3 Ion Exchange Mechanism

Heavy metal ions can replace exchangeable ions (e.g., Na^+, Cu^{2+}) in MOF-derived materials.Cu^{2+} in MOF-5-derived CuO/carbon exchanges with Pb^{2+} (0.8 mmol/g capacity), maintaining 92% removal in high salinity [20]. Na^+-doped materials selectively exchange with Sr^{2+} or Cs^+ (selectivity coefficient: 10^3–10^4), useful in nuclear wastewater treatment [22].

3. Recycling and Regeneration of MOF-Derived Nanomaterials

3.1 Main Regeneration Methods

Acids, alkalis, or chelators disrupt adsorbate–material bonds. For example, 0.1 M HCl desorbs Pb^{2+} from MOF-5-derived carbon with 92% efficiency and 85% capacity retention after 5 cycles [20]. EDTA desorbs Hg^{2+} from thiol-modified materials via stronger chelation (lgK = 21.8) [17]. Strong acids/alkalis may damage material structure.

Heating under inert or oxidative atmospheres (200–500°C) volatilizes or decomposes heavy metals. Zn^0/NC regenerated at 300°C in N_2 retains 90% Cr(VI) capacity after 10 cycles [19]. Temperature control is critical to avoid pore collapse or oxidation.

Also, applying voltage desorbs metals and regenerates active sites. N-doped carbon electrodes recover Au^{3+} with 98% desorption and 95% capacity retention; gold is recovered via electrodeposition [23]. This method is suitable for conductive materials.

3.2 Causes of Recycling Performance Attenuation and Optimization Strategies

3.2.1 Main Causes of Performance Attenuation

The performance of materials can decline due to several mechanisms. First, structural damage occurs when strong acids or alkalis corrode the material. For example, Fe_3O_4 dissolves in 0.5 mol/L NaOH, resulting in a 45% decrease in specific surface area [18]. Another cause is active site inactivation. Strong metal-binding interactions, such as Hg–S bonds, may lead to irreversible deactivation of catalytic sites, while organic fouling—such as humic acid deposition—can cover about 30% of active sites [17,24].

In addition, residual heavy metals contribute to attenuation. Incomplete desorption processes can block pores, and residual Pb^{2+} alone has been shown to reduce capacity by 25% [20]. Finally, component loss during repeated regeneration cycles is another critical factor. For instance, metal leaching may occur, with Fe losses of 5–8% after 10 cycles [25]. Together, these factors explain the progressive decline in performance during long-term use.

3.2.2 Optimization Strategies

Several strategies have been developed to mitigate these issues. Material reinforcement through compositing with carbon nanotubes, for example, reduces surface area attenuation from 30% to just 10% after five cycles [10]. Similarly, composite desorbents such as mixed EDTA/HCl solutions can achieve over 90% desorption efficiency while causing minimal structural damage [17].

Other effective measures include pretreatment processes, such as removing organics prior to operation, which can extend cycle life from 5 to 10 cycles [24]. Surface protection has also proven beneficial; coating with SiO_2 lowers acid-induced Fe leaching from 25% to below 5% [25]. Lastly, gradient regeneration strategies, such as mild alkaline pretreatment, reduce structural damage by approximately 40% [26]. Collectively, these optimization approaches help preserve material performance and prolong service life under repeated use.

4. Practical Application Cases of MOF-Derived Nanomaterials

4.1 Treatment of Electroplating Wastewater

A Chinese electroplating plant implemented ZIF-8-derived Zn^0/NC materials to address high-concentration Cr(VI) contamination (50-120 mg/L) in high-salinity wastewater (8-15% NaCl). The treatment system employed a fixed-bed reactor operating at 2 BV/h flow rate. The material demonstrated exceptional performance with an initial Cr(VI) adsorption capacity of 420 mg/g, significantly outperforming conventional activated carbon (85 mg/g) and ion exchange resins (180 mg/g). The material exhibited remarkable selectivity with separation coefficients of KCr/Ni = 45.2 and KCr/Pb = 38.7, enabling preferential Cr(VI) removal despite competing ions. After 12 consecutive regeneration cycles using thermal treatment at 300°C under N_2 atmosphere, the material maintained 90% of its initial capacity. The process achieved effluent Cr(VI) concentrations below 0.03 mg/L, under the national discharge standard of 0.5 mg/L. Economically, the operating costs were reduced to 2.5 CNY/m^3, representing 69% savings compared to activated carbon treatments [19,4].

4.2 Treatment of Mine Wastewater

A lead-zinc mine in Yunnan Province employed MIL-101(Fe)-derived Fe_2O_3 materials for comprehensive heavy metal removal from acidic mine drainage containing As(III) (50-80 mg/L), Cd^{2+} (10-20 mg/L), and Pb^{2+} (30-50 mg/L). The material achieved simultaneous removal through multiple mechanisms: surface -OH groups chelated Cd^{2+} and Pb^{2+}, while Fe^{3+} sites oxidized As(III) to As(V) with 98.5% efficiency, followed by precipitation as stable $FeAsO_4$. The adsorption capacity for As(III) reached 280 mg/g, substantially higher than conventional iron oxide hydroxides (120 mg/g). The integrated process enabled resource recovery through acid regeneration (0.05 M H_2O_2) and subsequent precipitation, producing 99.2% pure As_2O_3. This by-product generation offset approximately 30% of treatment costs, demonstrating the technology's economic viability. The treated effluent consistently met Class III national standards, with residual concentrations of As(III), Cd^{2+}, and Pb^{2+} below 0.02, 0.01, and 0.03 mg/L respectively [5]

4.3 Treatment of Electronic Waste Leachate

A specialized recycling facility in Guangdong Province utilized ZIF-67-derived nitrogen-doped carbon materials for precious metal recovery from electronic waste leachate containing Au^{3+} (5-20 mg/L) alongside toxic heavy metals. The material's pyridinic N sites (3.2 mmol/g density) enabled selective Au^{3+} adsorption and reduction to Au^0 with 99.8% efficiency, while carboxyl groups adsorbed Pb^{2+} and Cd^{2+}simultaneously.The process achieved a 95.2% gold recovery rate with a final product purity of 99.9%, outperforming traditional cyanide leaching methods. Continuous operation over six months demonstrated excellent stability, with the material maintaining 760 mg/g Au^{3+} adsorption capacity (95% retention). The integrated adsorption-calciation process (800°C under Ar atmosphere) facilitated direct gold ingot formation while volatilizing and capturing toxic heavy metals. The treatment ensured effluent quality compliance with national standards while creating significant economic value through precious metal recovery [21,6]

5. Challenges and Future Directions

Current challenges in this field include high preparation costs, as expensive precursors and complex synthesis processes hinder large-scale production; limited adaptability, since material performance often declines in complex wastewater containing organics or high salinity; engineering issues, as powder materials are difficult to handle and shaping them reduces efficiency; and a lack of standardization, where inconsistent testing conditions make it hard to compare different materials. Future development should therefore focus on low-cost synthesis by utilizing waste residues or biomass as precursors and developing continuous production methods such as fluidized bed pyrolysis. Enhancing stability through surface modification with hydrophobic or corrosion-resistant coatings will also be important. At the process level, integrating magnetic separation systems or composite membranes could enable continuous operation, while standardized evaluation protocols and performance metrics are needed for reliable comparison. Finally, multifunctional systems that combine these materials with oxidation or membrane technologies may provide more effective solutions for treating complex pollutants.

6. Conclusion

MOF-derived nanomaterials are promising for heavy metal removal and recycling due to their high capacity, selectivity, and regenerability. Key mechanisms include adsorption, reduction, and ion exchange. Practical applications demonstrate effectiveness in treating industrial wastewater and recovering valuable metals. However, challenges remain in cost, stability, and engineering integration. Future work should focus on scalable synthesis, performance optimization, and standardized evaluation to facilitate real-world implementation

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