Advances in the Treatment of Heavy Metal Ions in Wastewater by Adsorption Technology

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Abstract: With advancing industrialization, the discharge of heavy metal-containing industrialwastewater is increasing, a critical challenge in water pollution control. Heavy metal ions, with high toxicity, strong bioaccumulation and poor biodegradability, threaten ecosystems and human health severely. The adsorption method has attracted much attention for heavy metal removal due to its simple process, wide applicability and stable efficiency. This paper systematically reviews recent progress of adsorption technology in heavy metal wastewater treatment, focusing on adsorption mechanisms, adsorbent types and modification methods. It also summarizes application effects of typical adsorbents, discusses engineering application problems, and prospects future development, aiming to provide theoretical and practical references for heavy metal wastewater pollution control.

1 Pollution characteristics of heavy metal ions in wastewater

1.1 Origin and Hazards

Heavy metal ions in wastewater primarily stem fromindustrial activities such as metallurgy, electroplating,mining, chemical processing, electronics manufacturing, textile dyeing, and urban operations, as well as from pipeline corrosion and leachate from solid waste[4]. China's "Comprehensive Wastewater Discharge Standards" (GB 8978-1996) and "Pollutant Discharge Standards for Urban Wastewater Treatment Plants" (GB 18918-2002) set clear limits on heavy metals like mercury, cadmium, lead, and chromium, which are key targets for water management. These metals are highly toxic, environmentally persistent, and can accumulate in the food chain, posing risks to ecosystems and human health. Some also have mutagenic, teratogenic, and carcinogenic effects. Their difficulty in natural degradation and tendency to accumulate inwater and sediments contribute to long-term pollution, complicating wastewater treatment and environmental risk management[5,10].

1.2 Existing Forms

In wastewater systems, heavy metals exist in various forms, including free ions, inorganic and organic complexes, and particulate states, all influenced by physicochemical factors like pH, redox potential, dissolved organic matter, and coexisting ions [1]. According to GB 3838-2002 "Surface Water Environmental Quality Standards," these forms differ in migration, transformation, bioavailability, and toxicity. Free metal ions are highly mobile and biologically toxic, making them key targets in treatment[2]. In contrast, complexed or deposited metals are stable but may re-dissolve and cause secondary pollution under changing conditions.

2 Mechanism of Adsorption Technology in Heavy Metal Ion Treatment of Sewage

The adsorption process primarily relies on the physical or chemical interactions between the surface active sites of the adsorbent material and heavy metal ions. Common adsorption mechanisms include electrostatic attraction, ion exchange, surface complexation, and π-π interactions[4]. The adsorption behavior is significantly influenced by factors such assolution pH, ionic strength, and coexisting substances.Optimization of these parameters is crucial for enhancing adsorption efficiency and selectivity. Research continues to focus on developing novel adsorbents with high capacity and specificity for heavy metal removal.

2.1 Electrostatic Attraction

Electrostatic adsorption is one of the most basic mechanisms in the adsorption of heavy metal ions, which is driven by the Coulombic force between the surface charge of the adsorbent and the metal ions in the solution.When the solution pH exceeds the adsorbent's zero charge point ($pHbzc$), the surface of the adsorbent typically acquires a negative charge, which promotes the

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adsorption of positively charged metal ions, including Pb^{2+}, Cd^{2+}, and Cu^{2+}. The mechanism can be described as follows:

$$\equiv SO - +M2+ \rightarrow \equiv SOM + \quad (1)$$

Studies have demonstrated that the solvent pH is a critical factor in electrostatic adsorption, which constitutes the core mechanism of the electroadsorption system. In membrane electrolysis adsorption devices, negatively charged heavy metal oxygen anions such as Cr2O72- accumulate on the cathode chamber surface via electrostatic attraction, while Cr3+ and Fe3+ ions precipitate[5]. This highlights the critical role of interfacial charge effects in heavy metal ion removal in Figure 1.

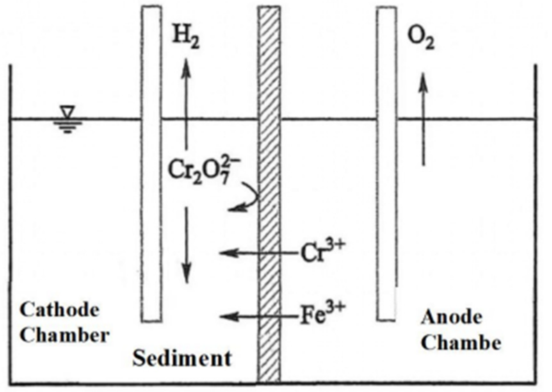

Figure 1. Diaphragm electrolysis recovery of chromium plating waste.

2.2 Ion Exchange

Ion exchange predominantly takes place on the surface of adsorbent materials possessing exchangeable cations, including natural zeolites, clay minerals, and specific modified biochar[6]. During the adsorption process, heavy metal ions in the solution exchange with pre-existing Na^+, K^+, or Ca^{2+} on the material surface. The reaction process can be represented as:

$$\equiv SO - Na + M^{2+} \rightarrow \equiv SO - M + Na^{+} \quad (2)$$

This mechanism exhibits high sensitivity to ionic concentrations in solutions. Studies indicate that the Cd^{2+} adsorption capacity of zeolites in high-concentration Na^+ or Ca^{2+} wastewater can decrease by 20%-40%. In engineering applications, ion exchange adsorbents are commonly employed during the pretreatment or advanced treatment stages of electroplating and mining wastewater[7]. Surface complexation serves as a critical chemical mechanism for heavy metal adsorption, where functional groups such as hydroxyl and carboxyl on the adsorbent surface form stable coordination complexes with metal ions.

$$\equiv SOH + M^{2+} \rightarrow \equiv SOM^{+} + H^{+} \quad (3)$$

This mechanism is characterized by high selectivity and stability. For example, amino-functionalized biochar shows a Cu^{2+} adsorption capacity of 150–200 mg g^{-1}, far exceeding that of pristine biochar. Within pH 3–6, Pb^{2+} uptake by biochar or graphene oxide can increase from <50 to >100 mg g^{-1}[3]. Surface complexation is strongly pH-dependent and is most stable under neutral to mildly alkaline conditions in Figure 2.

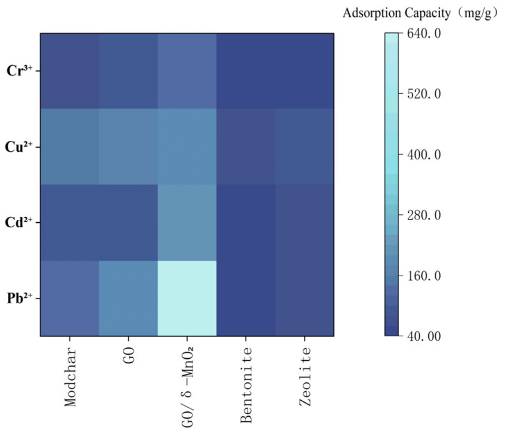

Figure 2. Adsorption capacity thermograms of heavy metal ions by different adsorbents.

2.3 Adsorption Mechanism Comparison and Guidance

The adsorption mechanism exhibits variations in accordance with different conditions. Under high pH conditions, electrostatic adsorption prevails as a result of the negative surface charge of the adsorbent, which promotes the adsorption of cations. In contrast, at low pH, surface complexation becomes more pronounced, especially for metal ions like Pb^{2+}. When the initial concentrations or the concentrations of competitive ions are high, ion exchange surpasses the previous two mechanisms owing to its strong adaptability[13]. Analyzing the dominant mechanism can optimize the design of adsorbents, enhancing the efficiency of heavy metal removal through material selection and the control of parameters such as pH and concentration. In conclusion, understanding the adsorption mechanisms under varying conditions is crucial for the development of efficient heavy metal removal strategies. By tailoring adsorbent properties and process parameters, we can significantly improve the effectiveness of water treatment and environmental remediation efforts. Future research should focus on the synthesis of novel materials and the exploration of new mechanisms to further enhance adsorption efficiency and selectivity.

3 Research Progress of Adsorbent Materials and Modification

3.1 Carbon based adsorbent

China researchers extensively study carbon-based adsorbents for removing heavy metal ions due to their large specific surface area, well-developed pore structure, and controllable surface groups. The team led by Wu Zhenghui at the Institute of Process Engineering studied graphene and its composites, discovering that graphene oxide enhances the adsorption of Pb^{2+} and Cd^{2+} through surface complexation and electrostatic interactions. The developed GO/δ-MnO_2 aerogel composite achieved a Pb^{2+}

adsorption capacity of 643.6 mg/g, surpassing traditional activated carbon[7]. A study by the team led by Zeng Guangming at Huazhong University of Science and Technology demonstrated that high-temperature carbonization and surface oxidation of biochar can increase the specific surface area and oxygen-containing groups, thereby improving the adsorption performance of Cu^{2+} and Zn^{2+}, confirming the critical role of surface functional groups in the performance of carbon-based adsorbents[8].

3.2 Norganic and Composite Adsorbent Materials

Inorganic adsorbents such as metal oxides and clay minerals have become key to China's heavy metal pollution control due to their stability and easy availability. Wang Yili's team found that acid-activated bentonite enhances Cu^{2+} adsorption capacity (40-60 mg/g) through ion exchange and surface complexation. However, the limited surface area of single inorganic adsorbents was overcome by Wu Zhenghui's team, who developed metal oxide/graphene composites that increase the specific surface area and improve the adsorption performance for multiple metals such as Pb^{2+} and Cd^{2+}[9]. These composites are structurally stable and reusable, making them suitable for wastewater treatment.Despite these advancements, the challenge of cost-effectiveness remains. Researchers are now focusing on the development of low-cost adsorbents derived from agricultural waste materials. For instance, Li Ming's group has successfully synthesized biochar from rice husks, which exhibits a remarkable adsorption capacity for arsenic (As) and mercury (Hg) due to its high carbon content and porous structure. The use of such biochar not only provides an environmentally friendly solution but also reduces the overall expenditure on adsorbent materials. Moreover, the integration of these natural and synthetic adsorbents into a hybrid system is being explored to optimize the removal efficiency of heavy metals from industrial effluents. This interdisciplinary approach aims to create a sustainable and efficient heavy metal removal process that can be widely implemented across various industries.

3.3 Challenges and Future Directions in Adsorbent Development

Although carbon-based, inorganic, and composite adsorbents exhibit promising performance in the removal of heavy metals, their practical application encounters challenges such as limited selectivity, high modification costs, and complex preparation processes. Moreover, low regeneration efficiency, poor stability, and the risks of secondary pollution further impede their adoption on an engineering scale[15]. Future research ought to concentrate on developing low-cost green modification techniques, improving material stability, and establishing multi-mechanism synergistic adsorption systems to promote the transformation of laboratory achievements into engineering applications. In conclusion, the advancement of heavy metal removal technologies hinges on overcoming these obstacles. By focusing on cost-effective and environmentally friendly modifications, enhancing the stability and regeneration of adsorbents, and creating systems that synergistically combine multiple adsorption mechanisms, we can bridge the gap between laboratory research and real-world applications. This will pave the way for more sustainable and efficient water treatment solutions, ultimately contributing to environmental protection and public health.

4 Kinetics and Isothermal Model of Adsorption Process

4.1 Adsorption Kinetics Models

The adsorption kinetics study analyzed the adsorption rate and control mechanism through pseudo-first-order and pseudo-second-order kinetic models. The satisfactory fitting of the pseudo-first-order kinetic model suggests that the adsorption process is predominantly governed by external diffusion or physicaladsorption. That is to say, the migration of solute tothe adsorbent surface serves as the rate-limiting step. The satisfactory fitting of the pseudo-second-order kinetic model implies that the adsorption process is primarily controlled by chemical adsorption or surface reaction. In other words, the adsorption rate is affected by electron sharing, coordination, or valence bonding.

4.2 Adsorption Isotherm Models

The isothermal behavior of adsorption is commonly described by the Langmuir and Freundlich models. The Langmuir model represents a single-layer adsorption, and its standard form is the Langmuir equation[11].

$$q = \frac{KPq_m}{1 + KP} \tag{4}$$

where q represents the equilibrium adsorption capacity (mg/g), q_m denotes the maximum monolayer adsorption capacity (mg/g), K is the Langmuir constant, and P refers to the equilibrium concentration.

The Freundlich model is suitable for heterogeneous surfaces and multilayer adsorption processes, with the empirical formula:

$$q_e = K_F \cdot C_e^{1/n} \tag{5}$$

K_F is the Freundlich adsorption constant, n is the adsorption strength parameter, and 1/n indicates the favorable degree of the adsorption process.

The Langmuir isotherm hypothesis posits that adsorption takes place on a homogeneous surface monolayer.A satisfactory fit of this isotherm implies the existence of homogeneous adsorption sites and feeble interactions[14]. In contrast, the Freundlich model is suitable for multi - layer adsorption on heterogeneous surfaces, which reflects the uneven distribution of adsorption energy. Discrepancies in model fitting can contribute to the determination of the adsorption mechanism, the evaluation of model limitations, and the guidance of adsorbent optimization.

5 Engineering Application Status of Adsorption Technology

New adsorbent materials for treating heavy metal wastewater are getting a lot of attention lately[9]. Modified carbon-based materials, with large surface area and oxygen groups, adsorb Pb^{2+} well. Composite adsorbents, blending multiple phases, provide better stability and recyclability for Cd^{2+} removal. Inorganic adsorbents like silicates and zeolites are cost-effective and available for Cr^{3+} removal, though their selectivity and capacity can be enhanced. Table 1 details the adsorption capacity and engineering applicability of these adsorbents, noting their strengths and weaknesses.

Table 1. Adsorption performance and engineering characteristics of different types of adsorbent materials for heavy metal ions

Adsorbent material type	Target ion	Maximum adsorption/ (mg·g^{-1})	Engineering Advantages	limitations
Modified carbon based material	Pb^{2+}	80–150	Large specific surface area	Limited regeneration cost
Composite adsorbent	Cd^{2+}	60–120	Good structural stability	Limited preparation complex
Inorganic adsorbent	Cr^{3+}	40–90	Wide range raw sources	Limited adsorption selectivity

6 Conclusion and Prospect

This study explored adsorption technology for the remediation of heavy metal-contaminated wastewater, achieving 90%–95% ion removal in electroplating, metallurgical, and chemical wastewaters. Nevertheless, its large-scale implementation remains constrained by issues such as adsorbent selectivity under complex water matrices, regeneration efficiency, and secondary waste management, which limit long-term sustainability and economic feasibility [11]. Further research is needed to address these challenges, focusing on the development of novel adsorbents with enhanced selectivity and regeneration capabilities, as well as strategies for minimizing secondary waste production.

Future research should therefore prioritize the development of cost-effective and robust adsorbents, the optimization of adsorption–desorption cycles, and the integration of adsorption with complementary treatment technologies, while ensuring strict compliance with discharge standards.Such advances are essential for translating laboratoryperformance into reliable engineering applications [12].In addition, it is imperative to focus on the scalability of adsorption processes to industrial levels, which involves the design of large-scale adsorption systems that can handle significant volumes of pollutants efficiently. Research should also address the long-term stability and regeneration capabilities of adsorbents to ensure their sustained effectiveness over time. The development of novel materials with enhanced selectivity for specific contaminants could further improve the efficiency and specificity of adsorption technologies. Moreover, the incorporation of real-time monitoring and control systems can optimize the performance of adsorption processes, making them more adaptive and responsive to varying water quality conditions. Collectively, these efforts will pave the way for more sustainable and efficient water treatment solutions, ultimately contributing to the protection of our environment and public health.

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