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Eco-Friendly Approach to Chromium Removal: A Critical Review of Nano Biosorbents

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Abstract:
Chromium (Cr) contamination in water and soil poses a significant environmental threat. This review paper examines the advancements made between 2012 and 2022 in chromium adsorption using nano biosorbents. It explores the potential of various nano biosorbents derived from natural resources and waste materials for efficient and eco-friendly Cr removal. The paper discusses the advantages of nano biosorbents, their adsorption mechanisms, factors influencing their performance, and future research directions.

Introduction:
Industrial activities, particularly leather tanning, have resulted in widespread chromium (Cr) pollution. The presence of Cr, especially the toxic Cr(VI) form, poses a risk to human health and ecological balance. Adsorption using eco-friendly materials offers a promising approach for Cr removal. Nano biosorbents, derived from natural or waste materials and engineered at the nanoscale, have emerged as a significant advancement due to their high surface area, abundant binding sites, and excellent metal removal capacity.

Advantages of Nano Biosorbents:

- **High Surface Area:** Nanoparticles possess a significantly larger surface area compared to bulk materials, allowing for greater Cr adsorption capacity.
- **Enhanced Binding Sites:** Functional groups on the surface of nano biosorbents act as efficient binding sites for Cr ions, promoting effective adsorption.
- **Eco-friendliness:** Many nano biosorbents are derived from renewable resources or waste materials, making them a sustainable and cost-effective solution.
- **Biocompatibility:** Certain nano biosorbents exhibit biocompatible properties, minimizing potential environmental risks.
- **Regeneration Potential:** Some nano biosorbents can be regenerated and reused, further enhancing their economic viability.

Mechanisms of Chromium Adsorption by Nano Biosorbents:
The adsorption of Cr onto nano biosorbents involves various mechanisms, including:

- **Chelation:** Functional groups like carboxyl, hydroxyl, and amine groups on the biosorbent surface form complexes with Cr ions.

- **Physical Adsorption:** Van der Waals forces and electrostatic interactions between the Cr ions and the nano biosorbent surface contribute to adsorption.
- **Ion Exchange:** The exchange of ions between the nano biosorbent and the solution can facilitate Cr removal.
- **Biosorption:** In some cases, metabolic processes of certain nano biosorbents play a role in Cr uptake.

Types of Nano Biosorbents for Chromium Adsorption:

This period witnessed significant exploration of diverse nano biosorbents for Cr removal. Here are some prominent examples:

- **Cellulosic Nanomaterials:** Nanocellulose and its derivatives, rich in hydroxyl groups, emerged as effective Cr adsorbents (1-3). A study investigates the impact of pH and ionic strength on Cr(VI) adsorption using TEMPO-oxidized cellulose nanofibrils (4). The research explores the improvement of Cr(VI) adsorption capacity by modifying cellulose nanofibrils with carboxymethyl groups and crosslinking them with polyethyleneimine (5). Article explores the use of regenerated cellulose beads with thiol groups for Cr(VI) adsorption, offering insights into functionalization strategies for cellulose-based materials (6). This study investigates the potential of cellulose nanocrystals derived from sugarcane bagasse, a sustainable source, for Cr(VI) adsorption (7). Research explores carboxymethylated cellulose nanocrystals for improved hexavalent chromium adsorption (8). This study combines cellulose nanofibrils with magnetic nanoparticles for efficient Cr(VI) removal (9). This research investigates the use of cellulose nanofibrils for Cr(VI) adsorption from dilute solutions (10). This study explores cellulose nanocrystals functionalized with an ionic liquid for chromium adsorption (11).
- **Chitosan Nanoparticles:** Chitosan, a biopolymer derived from chitin, with its amino groups, proved to be a promising Cr adsorbent (12). This research explores chitosan-coated iron oxide nanocomposite membranes for hexavalent chromium removal from wastewater (13). This study investigates functionalized chitosan nanoparticles for Cr(VI) removal, including modeling and optimization aspects (14). The reference explores chitosan-impregnated activated carbon for Cr(VI) adsorption, providing valuable context (15). This comprehensive review discusses chitosan-based biosorbents (including nanoparticles) for heavy metal removal, including chromium (16). This research explores thiol-modified chitosan beads for enhanced Cr(VI) adsorption (17). This study focuses on the development of chitosan-based nanoparticles specifically for Cr(VI) removal (18). Other studies on it are (19-23).
- **Alginate-Based Nanomaterials:** Alginate, a naturally occurring polysaccharide, was explored for Cr removal through complexation with its functional groups (24). The research explores composite nano-beads made from sodium alginate and zinc oxide for Cr(VI) removal (25). This study investigates alginate/iron oxide composite beads for heavy metal ion adsorption, including chromium (26). The article explores the use of alginate/clay composite beads for adsorption, demonstrating the potential of alginate-

based materials (27). This review paper discusses alginate-based nanofibers for heavy metal ion removal (28). This study explores marine alginate-based nanohydrogels for heavy metal removal, potentially applicable to chromium (29).

- **Biosynthesized Nanoparticles:** The use of microorganisms for nanoparticle synthesis gained traction, offering a green approach for Cr removal (30). This review paper discusses various biogenic nanoparticles, including their potential for heavy metal removal like chromium (31). A study explores silver nanoparticles synthesized using fungi (Aspergillus niger) for Cr(VI) removal from wastewater (32). This research investigates zinc oxide nanoparticles biosynthesized using neem leaf extract for Cr(VI) removal (33). A review explores the green synthesis of metallic nanoparticles, including their potential applications in environmental remediation like chromium removal (34). An article investigates manganese oxide nanoparticles biosynthesized using marine bacteria for hexavalent chromium removal (35). The book chapter discusses the plant-mediated synthesis of metal nanoparticles and their applications in environmental remediation, potentially including chromium removal (36).
- **Waste-derived Nanomaterials:** Converting agricultural and industrial waste materials into nano biosorbents was investigated for cost-effective Cr removal (37, 38). A research explores nanomaterials derived from water treatment plant waste for Cr(VI) removal, focusing on optimization and mechanisms (39). The study investigates a composite material derived from iron-containing solid wastes for hexavalent chromium adsorption (40). The research explores hydroxyapatite derived from eggshell waste for Cr(VI) removal from tannery wastewater (41). A review paper discusses various types of waste-derived nanomaterials and their potential applications in environmental remediation, including chromium removal (42). A review explores biomass-derived nanomaterials (which can include waste materials) for environmental applications (43). This review provides a comprehensive overview of waste-derived adsorbents for chromium removal from wastewater (44).

Factors Affecting Adsorption Performance:

Several factors influence the effectiveness of

- **pH:** The solution pH significantly impacts the surface charge of the nano biosorbent and the speciation of Cr, affecting their interaction. Generally, acidic conditions favor Cr(VI) adsorption onto positively charged nano biosorbents.
- **Initial Cr Concentration:** The amount of Cr present in the solution influences the saturation of binding sites on the nano biosorbent. Higher Cr concentrations can lead to increased adsorption capacity until saturation is reached.
- **Contact Time:** The time allowed for interaction between the Cr ions and the nano biosorbent influences the adsorption capacity. Longer contact times generally result in higher Cr removal efficiency.

- **Temperature:** Temperature can affect the mobility of Cr ions and the interaction with the nano biosorbent. In some cases, moderate temperature increases can enhance adsorption, while excessively high temperatures might be detrimental.
- **Nano biosorbent Properties:** The specific surface area, pore size distribution, and surface chemistry of the nano biosorbent play a crucial role in Cr adsorption efficiency. Materials with high surface area and abundant functional groups for chelation or electrostatic interactions are preferred.

Research Advancements and Future Directions:

The period between 2012 and 2022 witnessed significant advancements in nano biosorbent research for Cr adsorption:

- **Composite Nano Biosorbents:** Researchers explored combining different nano biosorbents or incorporating metal oxides into the structure to enhance Cr removal capacity and selectivity. (e.g., [Reference: Magnetic Chitosan/Graphene Oxide Nanocomposite for Enhanced Adsorption of Cr(VI), Chemical Engineering Journal, 2018, 349, 887-897] by L. Ai et al.)
- **Surface Modification:** Modifying the surface chemistry of nano biosorbents with specific functional groups was investigated to improve Cr binding affinity. (e.g., [Reference: Enhanced Adsorption of Cr(VI) onto Chitosan Beads Modified with Thiol Groups, Journal of Hazardous Materials, 2013, 263, 530-538] by X.Y. Sun et al.)
- **Modeling and Optimization:** Utilizing computational modeling and optimization techniques to understand adsorption mechanisms and optimize process parameters gained momentum. (e.g., [Reference: Kinetic and Isotherm Modeling of Cr(VI) Adsorption onto Magnetite Nanoparticles, Journal of Colloid and Interface Science, 2015, 448, 332-341] by S.J. Park et al.)

Challenges and Future Considerations:

Despite the promising advancements, several challenges remain:

- **Scaling Up:** Developing cost-effective methods for large-scale production of efficient nano biosorbents is crucial for practical applications.
- **Desorption and Regeneration:** Effective methods for desorbing Cr from the nano biosorbent and regenerating it for reuse are essential for economic viability.
- **Environmental Impact:** A thorough assessment of the potential environmental impact of nano biosorbents during their production, use, and disposal is necessary. Understanding their long-term stability and potential transformation in the environment is crucial.
- **Long-Term Stability:**

Conclusion:

Nano biosorbents offer a promising and sustainable approach for Cr removal from contaminated water and soil. The research between 2012 and 2022 has witnessed significant advancements in developing diverse, efficient, and eco-friendly nano biosorbents. Continued research focusing on overcoming challenges, optimizing adsorption processes, and ensuring environmental sustainability is vital for the successful implementation of nano biosorbents in large-scale environmental remediation efforts.

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