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BIOSORBENTS FOR THE REMOVAL OF TOXIC HEAVY METAL IONS FROM AQUEOUS SOLUTIONS

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Abstract Water pollution caused by toxic heavy metal ions is one of the important environmental problems associated with industrial, agricultural, mining and pharmaceutical activities. Heavy metals such as lead, cadmium, mercury, chromium and arsenic can persist in aquatic ecosystems and accumulate in living organisms because they are not biodegradable. Therefore, the development of effective, environmentally safe and economically feasible methods for removing heavy metal ions from contaminated water is of considerable scientific and practical importance. Biosorption is considered a promising alternative to conventional water treatment technologies because it uses biological materials capable of binding and removing pollutants from aqueous solutions. Biosorbents can be obtained from agricultural residues, plant biomass, microorganisms, algae, fungi, industrial by-products, animal wastes and natural polymeric materials. Their effectiveness is associated with the presence of functional groups such as hydroxyl, carboxyl, amino, sulfhydryl and phosphate groups, which interact with metal ions through ion exchange, complexation, electrostatic attraction, adsorption and precipitation mechanisms. This article reviews the main types of biosorbents, their physicochemical characteristics, mechanisms of heavy metal removal, factors affecting biosorption efficiency, and their potential applications in wastewater treatment. Particular attention is given to biosorbents based on natural fibers and silk waste as environmentally friendly materials for the removal of toxic metal ions from aqueous solutions.

Keywords biosorbent, biosorption, heavy metals, wastewater treatment, lead, cadmium, mercury, chromium, natural fibers, silk waste.

1. Introduction The contamination of water resources by toxic substances has become an important environmental and public health concern. Industrialization, urbanization and the development of chemical, metallurgical, mining, textile, pharmaceutical and agricultural industries have increased the discharge of pollutants into aquatic environments. Among these pollutants, heavy metal ions are particularly dangerous because they are persistent, non-biodegradable and capable of accumulating in organisms and food chains.

Lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr), arsenic (As) and several other metals can enter water systems through industrial wastewater, mining operations, metal processing, batteries, pigments, fertilizers, pesticides and other anthropogenic activities. Even at relatively low concentrations, some of these elements may cause adverse biological effects. For example, lead can affect the nervous system, cadmium can damage the kidneys, mercury can affect the nervous system, while certain forms of chromium and arsenic have significant toxicological importance. Conventional technologies for removing heavy metals from

wastewater include chemical precipitation, ion exchange, membrane filtration, electrochemical treatment, coagulation-flocculation and activated carbon adsorption. Although these technologies can be effective, they may have several limitations, including high operating costs, complicated equipment requirements, energy consumption and the production of secondary waste.

Biosorption has therefore attracted considerable attention as an alternative or complementary treatment method. Biosorption is a physicochemical process in which biological materials bind contaminants from aqueous solutions. Unlike active bioaccumulation, biosorption does not necessarily require living organisms or metabolic activity. Dead biomass and biological wastes can also demonstrate considerable sorption capacity.

The development of biosorbents from low-cost and renewable materials is especially attractive for sustainable wastewater treatment. Agricultural residues, plant materials, microbial biomass, algae, fungi, chitosan, cellulose-containing materials, wool, silk and other natural fibers can serve as biosorbents.

3. Chemical Structure and Functional Groups of Biosorbents

The sorption properties of biological materials are largely determined by their chemical composition and surface functional groups. Natural biomass commonly contains cellulose, hemicellulose, lignin, proteins, polysaccharides, lipids and other organic compounds. Functional groups present on the biosorbent surface can interact with metal ions through several mechanisms. Important groups include hydroxyl (–OH), carboxyl (–COOH), amino ($–NH_2$), sulfhydryl (–SH), phosphate and sulfate groups.

For example, a carboxyl group can participate in metal binding according to a simplified reaction:

$$R–COOH + M^{2+} \rightleftharpoons R–COO–M^{+} + H^{+}$$

Amino groups may also coordinate metal ions:

$$R–NH_2 + M^{2+} \rightleftharpoons R–NH_2–M^{2+}$$

The actual mechanism is usually more complex because several functional groups can simultaneously participate in the binding process.

Fourier-transform infrared spectroscopy (FTIR) is frequently used to investigate changes in functional groups after metal adsorption. Shifts in characteristic absorption bands can provide evidence of interactions between metal ions and functional groups on the biosorbent surface.

4. Biosorbents for Heavy Metal Removal

Heavy metal removal is one of the most extensively investigated applications of biosorption.

Lead. Lead is a highly important environmental pollutant because of its persistence and toxic effects. Many biological materials have demonstrated an ability to bind Pb^{2+} ions. Carboxyl and hydroxyl groups are among the important sites involved in lead binding. Cadmium. Cadmium contamination may originate from electroplating, batteries, pigments, mining and industrial processes. Biosorbents containing amino, carboxyl and hydroxyl groups can interact with Cd^{2+} ions. Mercury. Mercury is particularly important because of its high toxicity and ability to undergo transformations in the environment. Biosorbents containing sulfur-, nitrogen-

and oxygen-containing functional groups may be used for mercury removal. Chromium. Chromium exists in several oxidation states, but Cr(III) and Cr(VI) are particularly important in environmental chemistry. Their chemical behavior differs considerably. Cr(VI) species are generally present as oxyanions under many aqueous conditions, whereas Cr(III) commonly forms cationic and hydrolyzed species. Consequently, the mechanism of chromium removal depends on its oxidation state, pH and the chemical characteristics of the biosorbent.Arsenic. Arsenic may occur in different inorganic forms, particularly arsenite and arsenate. Because their charge and chemical behavior differ, arsenic removal often requires specially modified adsorbents or biosorbents.

5. Silk Waste as a Potential Biosorbent

Silk production generates various forms of waste, including damaged fibers, short fibers, cocoons, threads and other residual materials. These materials contain valuable protein components and can potentially be transformed into functional sorption materials. Silk is primarily composed of fibroin and sericin. Fibroin contains amino acids such as glycine, alanine and serine, while sericin is a hydrophilic protein containing various polar functional groups. The presence of amino, hydroxyl and carboxyl-containing groups makes silk-derived materials potentially useful for interaction with dissolved metal ions. Transformation of silk waste into a biosorbent can provide several environmental benefits: utilization of an industrial by-product; production of a renewable sorption material; reduction of solid waste; potential reduction of wastewater contamination; and development of a relatively low-cost treatment technology. Chemical modification can further increase the number or accessibility of active sites. For example, acid treatment, alkaline treatment or immobilization of a chelating reagent may alter the surface properties of silk fibers. An especially interesting approach is the immobilization of organic reagents capable of selectively binding heavy metals. Such modification can increase the affinity of the biosorbent toward particular metal ions and improve its analytical or purification performance.

6. Characterization of Biosorbents

Characterization is essential for understanding the structure and performance of biosorbents.

FTIR spectroscopy can identify functional groups and changes occurring after metal adsorption.

Scanning electron microscopy (SEM) can provide information about surface morphology and structural changes.

Energy-dispersive X-ray spectroscopy (EDS) can provide qualitative or semi-quantitative information about elemental composition and can help demonstrate the presence of metal ions on the biosorbent surface after adsorption.

UV–Vis spectroscopy can be useful when colored complexes are formed between metal ions and analytical reagents. It can also be applied to investigate the concentration of certain metal complexes.

pH measurements are essential for monitoring the chemical conditions of biosorption experiments.

The combination of these analytical methods provides stronger evidence for the proposed adsorption mechanism than the use of a single analytical technique.

7. Environmental and Practical Significance

The development of biosorbents from renewable resources corresponds to the principles of sustainable chemistry and circular economy. Instead of treating agricultural or industrial biomass as waste, it can be converted into a useful material for environmental remediation.An effective biosorbent should ideally have: high adsorption capacity; good selectivity toward target pollutants; rapid adsorption kinetics; chemical and mechanical stability; low production cost; availability of raw materials; possibility of regeneration; and minimal secondary pollution. For practical wastewater treatment, laboratory adsorption capacity alone is not sufficient. The stability of the biosorbent, regeneration efficiency, behavior in real wastewater and competition between different ions must also be investigated. Real wastewater usually contains several metal ions and organic or inorganic compounds. Therefore, experiments using multicomponent systems are important for determining the practical selectivity of a biosorbent.

8. Conclusion Biosorption represents a promising approach for the removal of toxic metal ions from contaminated water. Biological materials contain numerous functional groups capable of interacting with metal ions through ion exchange, complexation, electrostatic attraction, surface adsorption and precipitation. The use of low-cost biomass and industrial wastes as biosorbents offers both environmental and economic advantages. Among different natural materials, protein-containing fibers and silk waste deserve particular attention because their chemical structure provides potentially active sites for metal binding. The efficiency of biosorption depends on pH, contact time, biosorbent dose, initial metal concentration, temperature, particle size and the presence of competing ions. FTIR, SEM/EDS, UV–Vis spectroscopy and adsorption modeling can be effectively combined to characterize biosorbents and investigate their mechanisms.Overall, the development of environmentally safe biosorbents from renewable resources may contribute to sustainable wastewater treatment and the reduction of toxic metal contamination. Further research should concentrate on surface modification, selectivity, regeneration, multicomponent adsorption and continuous-flow systems to facilitate practical application.

Table 1. Major groups of biosorbents and their characteristics

Biosorbent group	Examples	Main functional groups	Potential applications
Plant biomass	Sawdust, rice husk, agricultural residues	–OH, –COOH	Heavy metal removal
Algal biomass	Brown, green and red algae	–COOH, –OH, –SO_3H	Pb, Cd, Cr, Cu removal
Fungal biomass	Aspergillus, Penicillium biomass	–NH_2, –OH, –COOH	Metal and dye removal
Bacterial biomass	Bacterial cells and residues	–COOH, –NH_2, phosphate groups	Metal and dye removal
Natural polymers	Chitosan, cellulose, lignin	–OH, –NH_2, –COOH	Metal ions and dyes

Biosorbent group	Examples	Main functional groups	Potential applications
Animal-derived materials	Wool, silk, bone-derived materials	$–NH_2$, –COOH, –OH	Heavy metal removal
Industrial/agricultural wastes	Fruit peels, husks, fibers	Various oxygen-containing groups	Low-cost wastewater treatment

Table 2. Main factors affecting biosorption

Factor	Effect on biosorption
pH	Determines surface charge and metal speciation
Initial metal concentration	Influences the driving force of adsorption
Biosorbent dose	Determines the number of available active sites
Contact time	Controls the approach to adsorption equilibrium
Temperature	Can affect diffusion and adsorption thermodynamics
Particle size	Influences surface area and mass transfer
Ionic strength	May influence competition between ions
Presence of competing metals	Can reduce selective adsorption
Surface modification	Can increase the number of active sites

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