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Review Article

Bacterial Exopolysaccharide mediated heavy metal removal: A Review on biosynthesis, mechanism and remediation strategies

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ABSTRACT

Heavy metal contamination has been recognized as a major public health risk, particularly in developing countries and their toxicological manifestations are well known. Conventional remediation strategies are either expensive or they generate toxic by-products, which adversely affect the environment. Therefore, necessity for an environmentally safe strategy motivates interest towards biological techniques. One of such most profoundly driven approach in recent times is biosorption through microbial biomass and their products. Extracellular polymeric substances are such complex blend of high molecular weight microbial (prokaryotic and eukaryotic) biopolymers. They are mainly composed of proteins, polysaccharides, uronic acids, humic substances, lipids etc. One of its essential constituent is the exopolysaccharide (EPS) released out of self defense against harsh conditions of starvation, pH and temperature, hence it displays exemplary physiological, rheological and physio-chemical properties. Its net anionic makeup allows the biopolymer to effectively sequester positively charged heavy metal ions. The polysaccharide has been expounded deeply in this article with reference to its biosynthesis and emphasizes heavy metal sorption abilities of polymer in terms of mechanism of action and remediation. It reports current investigation and strategic advancements in dealing bacterial cells and their EPS in diverse forms – mixed culture EPS, single cell EPS, live, dead or immobilized EPS. A significant scrutiny is also involved highlighting the existing challenges that still lie in the path of commercialization. The article enlightens the potential of EPS to bring about bio-detoxification of heavy metal contaminated terrestrial and aquatic systems in highly sustainable, economic and eco-friendly manner.

Contents

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1. Introduction

Heavy metals (Pb^{2+}, Cr^{2+}/Cr^{3+}, Cd^{2+}, Ni^{2+}/Ni^{4+}, Zn^{2+}, Cu^{2+}, Hg^{2+} etc.) are natural elements with relatively high density compared to water [94]. In trace amounts some of the heavy metals such as Cu^{2+}, Zn^{2+}, Fe^{2+}/Fe^{3+} etc. are essential for numerous vital biological processes in human physiology. However, toxicological manifestations arise at even slightly higher concentrations. Owing to their large scale industrial applications (pharmaceuticals, pesticides, plastics, rubbers, tanneries, organic chemicals and wood products) [46], occurrence of free forms of heavy metals in terrestrial as well as in aquatic system is on rise. Moreover, the non-biodegradable nature of heavy metals ensures its prolonged presence in the environment. Their high aquatic solubility triggers bioaccumulation and biomagnifications which eventually leads to insidious and irreversible health hazard (including potential carcinogenicity) even in very minimal concentration range of about 1 mg/L. Further they result in adverse environmental impacts because of their recalcitrant and non-biodegradable nature. Besides, certain environmental conditions favor their transformation from lower to higher toxic state like in case of mercury [99]. While talking about accessibility, precious metal ions in utilizable form are depleting day by day so their regeneration and extraction from all the potential sources is highly desired.

1.1. Toxicological manifestations of some heavy metals

Different heavy metal ions have different mechanisms of toxic infestations. Oxidative stress out of free radical imbalance (lead), harmful thiol or methyl derivative formation (mercury, arsenic, chromium), cofactor or metal ion replacement (aluminium, cadmium), cell membrane permeation, disturbance in ion channels, DNA and protein damage (chromium VI), binding to vital proteins and causing further discrepancies (cadmium), corrosive effects, saturation, organ penetration and lipid peroxidation (iron) are some of the predominant ones [35]. Recommended arsenic maximum concentration level by WHO in drinking water is 10 μg/L [102]. Beyond this the inorganic arsenic ion accumulation in living tissues instigates bronchitis, cancer, dermatitis, hypo 1 kerotosis, livercirrohosis, mental disturbance, ulcer etc in individuals [3,77]. Cadmium ions can cause chronic toxicity leading to proteinurea and lung emphysema upon air borne exposure. In higher dosage it causes acute toxicity with headaches, nausea, diarrhoea and osteomalasia. Chromium ion toxicity is recognized in its hexavalent form, its incursion in body at occupational level can cause skin ulcers, while inhalation can lead to dermatitis. Chronic exposure causes asthma and can possibly result in cancer too. Cobalt is one of the essential elements required for functioning of vitamin B_{12} whose recommended dietary intake itself is 6 μg. Aerial intake of cobalt ions at concentration beyond 0.005 mg/m^3 may lead to chronic lung ailments like asthama, pneumonia etc. Whereas dietary intake beyond 0.14–0.15 mg/kg of body weight results in heart complications and exposure to gamma rays can be lethal and carcinogenic. Overexposure to copper ions (beyond systemic excretion limit) results in hazards of immune system, kidney and liver distress, gastrointestinal ailments, anemia and even indirect onset of oxidative stress. Effects of lead toxicity are varied and widespread from hematopoietic, hepatic and renal system to even nervous system. Exposure at about 400–600 μg/L can also lead to chronic toxicity which is characterized by persistent vomiting, encephalopathy, lethargy, delirium, convulsions and coma if not attended timely [22].

So far, the mainstay treatment regimes for remediation of heavy metals ions include methods like coagulation, chemical precipitation, electrodialysis, evaporative recovery, floatation, flocculation, ion exchange, nanofilteration, reverse osmosis, ultrafiltration etc. [46,98]. Although effective, these methods are usually expensive due to high energy and reagent requirements. Moreover, they generate large amount of toxic sludges and byproducts, which pollutes the environment. Many a times they may result in incomplete and unpredictable (quantitative removal cannot be accurately estimated, depends on several factors dealt later in the article) metal ion removal [5,27]. Hence, there is an imperative need to devise effective, efficient, economic and environmentally safe strategies which can minimize the heavy metal ion concentration from toxic to safe limits in environment.

Sorption with specific reference to metal ions can be defined as any phenomenon that involves their association (ranging from electrostatic to covalent) with peripherally available one or more functional groups on sorbent material. When the sorbent involved in such reaction is a biological agent, the phenomenon is defined as biosorption. Prokaryotic as well as eukaryotic microbial biomasses (living or dead cells), like bacteria, fungi, yeast and few microalgae are such emerging candidates of biosorption which can uptake and reduce heavy metal ion concentration from contaminated water sources in eco-friendly manner [3,15,78].

Talking specifically of bacterial cells, heavy metal ions in both particulate as well as in soluble form can potentially be accumulated by intact bacterial cells (live or dead) and their byproducts. Extracellular polymeric substances are such complex blend of high molecular weight microbial biopolymeric secretory byproducts. Basically they contain proteins, polysaccharides, uronic acids, humic substances, lipids etc. Their most essential constituent, having ion sequestration capability, is extracellular polysaccharides or exopolysaccharide (EPS). Primarily it is composed of complex high molecular weight organic macromolecules like polysaccharide along with smaller proportions of protein and uronic acid [12,48].

These biosynthetic polymers can exist either as attached capsular polysaccharide (CPS) or as slime upon microbial surfaces [105].They are produced out of self defense against environmental stress which not only protect cells against dewatering or toxic substances but serves as a carbon and energy source as well [88]. Compositionally they are often seen to be polymerized of hexose sugar moieties and exist as both homo or heteropolysaccharide (Table 1) Czaczyk and Myszka, 2007.

These water-soluble glycopolymeric biomolecules display exemplary physiological, rheological and physio-chemical properties, that make them suitable for several clinical, industrial and environmental applications [12]. One such prospective application emerges from their ability of exhibiting physical defense [43]. Bacterial cell finds a way to protect itself from the infiltration of toxic metal ions by covering its peripheral surface with a shield of EPS. Structural and compositional makeup of EPS favors the sequestration of metal ions and hence obstructs them from penetrating the cell surface. Because of this property, in past few