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A comprehensive review on cyanobacteria-based phycoremediation: An eco-friendly approach for heavy metal removal from contaminated water bodies

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Abstract
Phytoremediation is a new emerging tool for reducing the concentrations and toxic effects of contaminants in the environment with the help of plants and associated soil microbes. Phytoremediation is acknowledged as an efficient and affordable method for restoring the environment. Aquatic contamination is increasing day by day due to different natural and anthropogenic activities leading to soil, water and food chain contamination. These activities are hazardous to the climate. Various types of potential approaches are beneficial for removing toxicants from aquatic ecosystems among them phycoremediation is a low-risk and environmentally friendly clean-up method where algae are used to decontaminate the environment. Cyanobacteria (blue-green algae) are more effective, affordable and eco-friendly alternative to conventional physico-chemical remediation methods. Due to their tremendous adaptability and effective protective mechanisms against various abiotic stresses, cyanobacteria occur in diverse habitats, such as terrestrial and aquatic, even at extreme climatic conditions and polluted waters. Many cyanobacterial species are effective in removing heavy metals from aquatic ecosystems. This review highlights the role of cyanobacteria in eco-friendly detoxification and the effective degradation of various types of toxicants present in different water bodies.

Keywords: Phytoremediation, phycoremediation, cyanobacteria, toxicants and contamination

Introduction

Heavy metals are toxic, non-biodegradable and persistent environmental pollutants that impacts negatively on all life forms, including humans and destroy ecological equality. The hazardous effects of heavy metals on living organisms are attributable to their action on many physiological and biochemical processes, as well as, biomolecules and structures in living organisms, including human beings. In humans, it causes various types of serious disorders related to the hepatic, renal, respiratory and gastrointestinal systems. It also disturbs the life cycle of zooplanktons and phytoplanktons [1]. Elevated concentrations of the heavy metals inhibit plant metabolism, leading to various effects depending on the type of heavy metal, its concentration applied and the environmental conditions during stress. Excessive contamination of aquatic environments with toxic heavy metals such as cadmium (Cd), mercury (Hg), lead (Pb), nickel (Ni), chromium (Cr), arsenic (As), silver (Ag), copper (Cu) and zinc (Zn) is due to the discharge of industrial waste products and other anthropogenic activities [2].

Cyanobacteria are primitive, morphologically diverse and widely distributed group of photosynthetic prokaryotes that resemble Gram-negative bacteria in cellular structure and green plants in oxygenic (O_2-evolving) photosynthesis [3]. Cyanobacteria are classified in class Oxyphotobacteria in the eubacterial division Gracilicutes by bacteriologists whereas, phycologists classified it in class Cyanophyceae or Myxophyceae in the algal division Cyanophyta [4, 5]. Due to their unique physiology and metabolism, cyanobacteria are considered to be highly productive and efficient biological systems. Both ecologically and economically, they are important organisms with varied implications and applications for the ecosystem [6]. Because of their potential and valuable role in multiple areas such as agriculture, aquaculture, human nutrition, bioenergy, biofuels, pharmaceuticals and pollution control, cyanobacteria are getting special attention worldwide for removal of toxicants from aquatic habitats [7]. Many cyanobacterial species can tolerate excessive concentrations of various toxic heavy metals due to the presence of resistance and well-developed defense mechanisms against heavy metals. They also possess efficient heavy metal removal capabilities from aquatic water bodies. Cyanobacterial species such as *Oscillatoria* sp. H1, *Sargassum muticum*, *Synechocystis*, *Spirulina*, *Nostoc minutum*, *Turbinaria turbinata*, *Caulerpa scalpelliformis*, *Pseudanabaena catenata*, *Anacystis nidulans*, *Lyngbya whollei*, *Aphanothece flocculosa*, *Nostoc* PCC 7936, *Gracilaria edulis*, *Lyngbya majuscula* have prominent metal sorption capacity than simple biomasses due to having large surface area [8].

The present review article is designed to make an overview study of the role of cyanobacteria in the removal of toxic heavy metals from water bodies because cyanobacteria have some additional advantages over other microorganisms such as their simple nutrient intake and more surface area with high binding affinity.

Heavy metals as toxicants in aquatic ecosystems

Heavy metal refers to any metallic chemical element that has a relatively high maximum density and is toxic or poisonous at low concentrations such as mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl) and lead (Pb). Heavy metals are commonly natural components of the earth's crust which cannot be degraded or destroyed. Heavy metals cause negative impacts on biotic fauna in aquatic ecosystems due to bioaccumulation which means an increase in the concentration of toxicants in food chains. They also affect the natural activities of ecosystems that limit the growth of biotic fauna.

Weast (1984) has classified 53 elements as heavy metals out of 90 naturally occurring metals, of which 17 heavy metals are available for living cells and important for the growth and development of organisms and ecosystems. Of these Fe, Mo, and Mn are essential micronutrients and some of them are toxic elements such as Zn, Ni, Cu, V, Co, W and Cr with high or low importance as trace elements and As, Hg, Ag, Sb, Cd, Pb and U do not have any specific known functions for plant growth and metabolism and shows less toxicity to plants and microorganisms growth [9, 10]. Low concentrations of heavy metals are deleterious for plant growth, inhibiting the physiological metabolism in plants. The accumulation of heavy metals by plants and further accumulation along the food chain has serious hazardous effects on animal and human health. Pollutants like heavy metals in aquatic ecosystems lead to the production of reactive oxygen species (ROS) that can cause death to fish and other aquatic organisms (zooplanktons and phytoplanktons) [11].

Heavy metals can enter into water bodies through discharge of industrial and domestic wastes. Acid rain can dissolve soils which releases heavy metals that flows into streams, lakes, rivers and groundwater. Heavy metals enter into humans through food, water, air or absorption through the skin when they come in contact with agriculture and manufacturing, pharmaceutical, industrial or residential settings. Ingestion is the most common way of exposure in children. Industrial exposure is responsible for various disorders in adults [12].

Heavy metals disturb the activity of various metal-sensitive enzymes essential for plant growth such as alcohol dehydrogenase, nitrogenase, nitrate reductase, amylase, phosphatase and ribonuclease (hydrolytic enzymes) and phosphoenolpyruvate carboxylase and ribulose-1, 5-bisphosphate carboxylase (carboxylation enzymes) [13]. These heavy metals adversely affect various types of life activities in fishes such as gamete formation, sperm quality, embryonic development, delay hatching and cause physical disturbance too that may even lead to the death of newly hatched larvae (fries) [14].

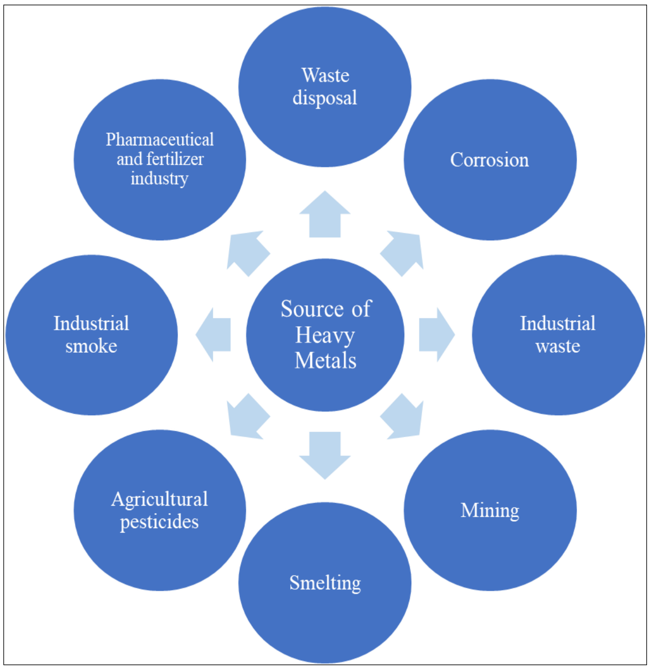

Fig 1: Sources of Heavy Metals.

Toxicants in aquatic ecosystems are capable of causing different types of indirect ecological effects that can be even more significant than the toxic effects of a contaminant. Some metals such as As, Cd, Hg, Pb or Se are not required for plant growth, because these do not demonstrate any physiological function in plants and remaining such as Co, Cu, Fe, Mn, Mo, Ni and Zn are essential elements required for normal growth and metabolism of plants, but these elements can be harmful when their concentration exceeds optimal values [15]. Contamination of aquatic habitats with heavy metals may cause devastating effects on the ecological balance of the aquatic environment and also disturb the diversity of aquatic organisms [16].

Toxic heavy metals enter into the human body through the aquatic food chain and cause various types of disorders. All heavy metals have specific target organs like Cd toxicity targets liver, placenta, kidneys, lungs, brain and bones. Depending on the severity of exposure, the common symptoms of toxicity include nausea, vomiting, abdominal cramps, dyspnoea and muscular weakness. Severe exposure may result in pulmonary oedema and also death. Pulmonary effects such as emphysema, bronchiolitis and alveolitis and renal effects may occur due to sub chronic inhalation or exposure of cadmium and its compounds. Cd has been associated to a lesser or greater extent with many clinical disorders, such as anosmia, cardiac failure, cancer, cerebrovascular infarction, emphysema, osteoporosis, proteinuria and cataract formation in the eyes [17, 18].

Toxic heavy metals

Arsenic (As): - Arsenic is released into the water and soil by the smelting processes of copper, zinc and lead, as well as, by the manufacturing of chemicals and glasses. Arsenic gas is released from the manufacturing units of pesticides too. Arsenic is also found in water bodies that affect plant growth.

Lead (Pb): Every year, industries produce about 2.5 million tons of lead throughout the world. Lead is mostly used in batteries, pesticides and also used for cable coverings, plumbing, fuel additives, in paint pigments, PVC plastics, x-ray shielding and crystal glass production [13]. It is one of the most toxic substances accumulating in aquatic ecosystems. Removal of lead by cyanobacteria was reported under laboratory conditions by Raungsomboon (2008). He reported that a cyanobacterium *Gloeocapsa* is capable of growing at the concentration range between 0-20 mg/L. The maximum accumulation of lead by *Gloeocapsa* was reported to be 232.56 mg/g [19].

Mercury (Hg): Mercury is formed naturally in the environment by degassing of the earth's crust from volcanic emissions. Significant production of mercury occurs through mining operations, chlor-alkali plants and paper industries [20]. Atmospheric mercury spreads across the world by winds and returns to the earth in the form of rainfall and bioaccumulates in fishes and aquatic food chains that reduces the life span of aquatic organisms [21]. Mercury is also used in thermometers, thermostats and dental amalgams.

Cadmium (Cd): Cadmium has been reported as a highly toxic metal and is a hazard to the environment. It is a by-product of mining and smelting of lead and zinc. Cadmium is used for nickel-cadmium battery formation, PVC plastics and paint pigments. It is also dominant in soil and water where it enters through insecticides, fungicides, sludge and commercial fertilizers used in agriculture [12]. It has been reported in a phytoplankton species belonging to the diatoms *Thalassiosira weissflogii*, where the addition of Cd in cultures enhanced the growth and led to the expression of a carbonic anhydrase enzyme with properties different from the normal enzyme of Zn-replete cultures [22].

Copper: Copper is an essential micronutrient for plant growth and metabolism and has a specific role in activity of metalloenzymes and photosynthesis-related plastocyanin, but in excessive concentrations affects several physiological and biochemical processes such as changes in nitrogen metabolism with reduction of total nitrogen and increase of free amino acids [23, 24].

Role of cyanobacteria in phycoremediation

Cyanobacteria are not only used as a food product for decades but also play an important role in industry and environmental remediation. It also serves as a very good source of essential nutrients such as vitamins, minerals, polyunsaturated fatty acids and rich in protein content. Cyanobacteria are nominated as green eco-friendly bioremediation tool in the current scenario due to their potential role in wastewater treatment for the removal of toxicants from water bodies. Several strains of cyanobacteria were reported to accumulate and detoxify different types of organic and inorganic pollutants [25]. Cyanobacteria and algae have photosynthetic pigments, necessary to fix atmospheric nitrogen to improve the productivity of soil and crops. Fe, Pb, Cd, Zn, Cu and Mn can be removed by cyanobacterial species from sewage wastewater very efficiently with removal rates ranging between 14.9% to 88.5%. In general, the highest percentage of reduction of heavy metals from the sewage sample was recorded by *Aspergillus oryzae* [26].

Cyanobacteria have recently been raised as experimental organisms of environmental biotechnology programmes not only because of their role in soil fertility but also due to their potential to remove heavy metals from polluted sites and their active participation in the reclamation of degraded soils. Cyanobacteria, in addition to enrichment of soil, play a significant role in suppressing weeds, degradation or transformation of heavy metals into less or non-toxic forms. Cyanobacteria are also capable of degrading naturally occurring hydrocarbons [27] and xenobiotics [28] present at the contaminated sites.

Cyanobacteria are capable of degrading or detoxifying many gaseous, solid and liquid recalcitrant pollutants including those of natural and xenobiotic origins, such as carbon dioxide, nitrogen, phosphorous, phenolics, pesticides, antibiotics, melanoidin, lignin and detergents [29]. Toxic heavy metals can also be removed from effluents by the processes of bioaccumulation and biosorption [30]. Many species of cyanobacteria can synthesize metal-binding proteins 'metallothioneins' that help organisms in the sequestration of toxic metal ions. Metallothioneins contain many thiol-containing cysteine residues that are involved in metal binding. These proteins act as defense mechanisms in the organism by binding metal ions intracellularly [31]. Certain cyanobacteria produce bioflocculants that protect them from the toxic effects of heavy metals. Bio-flocculants are extracellular macromolecules capable of clarifying turbid water and may remove dissolved nutrients from the water column thereby accelerating the heterotrophic activity in the sediment region. Bioflocculants are characterized by the presence of numerous negatively charged binding sites that empower the cyanobacteria in the removal of heavy metals from polluted sites. *Oscillatoria* sp. is effective in removing Pb, Cd, Cu, Zn, Co, Cr, Fe and Mn from water by producing extracellular bioflocculants when exposed to heavy metal stress [32].

The use of microorganisms including cyanobacteria in the removal of heavy metals from contaminated sites has several potential advantages such as rapid kinetics of the metal removal, utilization of naturally abundant renewable biomaterials and the possibility to treat water containing multiple metals. Capability of fixing atmospheric nitrogen along with atmospheric carbon make cyanobacteria suitable as bioremediating agents.

Table 1: List of cyanobacterial species for phycoremediation of heavy metals from aquatic ecosystems.

S.No.	Cyanobacterial species	Heavy metals	Removal efficiency	References
1.	*Spirulina fusiformis*	Cr VI	93-99%	[33]
2.	*Microcystis* sp.	Cd II, Cu II, Cr VI	24–76%	[34]
3.	*Microcystis* sp.	Sb III	87%	[35]
4.	*Cyanospira capsulata* ATCC43193, *Cyanothece* (ET5, TI4, PE14, VI22, CE4) and *Nostoc* PCC7936	Cr VI	50%	[36]
5.	*Cyanospira capsulate*	Cu II	96%	[37]
6.	*Nostoc* PCC7936	Cu II	79%	[37]
8.	*Anabaena doliolum*	Cd II	69-92%	[38]
9.	*Nitzschia closterium, Navicula incerta*	Pb II	74%	[39]
10.	*Synechococcus* sp. PCC 7942	Hg II	50%	[40]
		Pb II	45%	
		Cd II	34%	
11.	*Tolypothrix tonica*	Cu II	86.12%	[41]
		Zn II	94.63%	
12.	*Limnococcus* sp.	Cr VI	63.23%	[42]
13.	*Nostoc muscorum*	Cu II	96.42%	[43]
		Zn II	71.3%	
		Pb II	96.3%	
		Cd II	84.04%	
14.	*Oscillatoria annae*	Cd II, Pb II	85%	[44]
15.	*Arthrospira platensis*	Cd II	97%	[45]
		Pb II	91%	

Cyanobacteria gained momentum for phycoremediation of wastewater because firstly, they maximize the O_2 content of water through photosynthesis and perform bioremediation of toxicants including heavy metals. Secondly, it plays a significant role in distressing the biological oxygen demand (BOD), chemical oxygen demand (COD), turbidity, minerals and microbes. Thirdly, can also be used either as axenic cultures or as mixed cultures both offering distinct advantages. Some strains of cyanobacterial species are tolerant towards extreme temperatures both low and high, acidic pH, high salt concentrations and heavy metals, which makes them a prominent source for wastewater treatment plants [46]. Cyanobacterial biomass can retain 30 % of chromium and 65 % of lead from laboratory wastewater and 86 % of chromium and 62 % of lead from synthetic solutions [47]. Therefore, Cyanobacteria are used as effective bioremediation agents in wastewater.

Some reports stated that cyanobacterial species have been used as absorbent agents in heavy metal removal such as cadmium(Cd), lead(Pb) and chromium(Cr). The performance of heavy metal removal by *Aspergillus oryzae* was higher in accumulating the metal ions from sewage compared to the other studied cyanobacteria [26].

The removal of toxic metal ions from the polluted effluent by using cyanobacteria has taken much importance because of their small size and have high surface area-to-volume ratio which provides a large contact area for metal binding. The biosorption processes have been studied extensively using microbial biomass as biosorbent for heavy metal ions removal because of the adherent advantage of mass cultivation. All of these desirable physiological characteristics and applications have made it as a model organism to understand nitrogen metabolism. The study provides important recent advances in the characterization of nitrate assimilation and bioremediation potential. *Spirulina platensis* contains key genes such as nirA, narB and nrtP, which are involved in nitrate and nitrite reduction, contributing to its efficiency in nitrogen assimilation and pollutant removal from the environment [48].

Cyanobacteria are ubiquitous and can grow in a rich polluted environment and thereby adopt resistance genes against toxic heavy metals. Cyanobacteria and microalgae have specific properties to eliminate toxic pollutants from industrial wastes due to their good biosorption, biodegradation and transformation capacities. Cyanobacteria degrade a wide range of toxicants by modifying metabolic processes and secreting various types of metabolites into their surroundings. Degradation processes for heavy metals and metalloids are enhanced due to the co-metallic nature of cyanobacterial exopolysaccharides, Cyanobacteria significantly cleaned contaminated sites that are polluted with heavy metals, phenolic compounds, dyes, polycyclic aromatic hydrocarbons (PAHs) and petroleum by-products [49]. Cyanobacteria currently emerge as potentially eco-friendly, require less manpower and are low-cost remediators with nutritional requirements. It has a Remarkable ability to adapt to a wide range of environmental conditions by modifying their metabolic processes.

Conclusion

Contaminated environment has become common issue as global threat to ecosystem and has impact on plants, humans, all aquatic fauna and associated socio-economic loss. Phycoremediation is a new emerging suitable and potent tool for remediating toxic materials present in aquatic systems. Selected cyanobacterial species exhibit excellent bioremediation abilities toward heavy metals contaminating water or wastewater even at high concentrations. This strategy can be efficiently used for decontaminating wastewater effluents, as well as, natural aquatic ecosystems. Phycoremediation with cyanobacteria is not only limited to the protection of the received environments but also helpful in recovering minerals and reuse the treated compatible wastewater for irrigation of non-edible crops. Cyanobacteria are better candidates for different human-oriented developmental processes including agricultural, industrial or environmental programs to maintain ecosystem equality. Therefore, the present study will provide baseline data regarding evaluating the effects of heavy metal toxicity on aquatic fauna and also provide the outline study of phycoremediation with the help of cyanobacterial species.

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