Sughosh Madhav · Gyan Prakash Gupta
Rajiv Kumar Yadav · Ritu Mishra
Eric van Hullebusch *Editors*

Phyto-remediation

Biological Treatment of Environmental Pollution

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Preface

Serious environmental risks are brought on by the rapid demographic and industrial development. As a result of industrial operations such as ores mining, gas emission, pesticide application, and municipal waste generation, humans have long added significant amounts of pollutants to the soil, water, and atmosphere biotopes. These contaminants may build up in food systems, harming plants and animals as well as humans (damage to the endocrine system, impact on immunity, neurological disorders, cancer, etc.). Phytoremediation is an energy-efficient and eco-friendly technique for the remediation of heavy metals and other toxic elements from water air and soil. This technique is the need of the hour as environmental contamination is a serious concern for the human being. New advancements in the field of phytoremediation make it more appropriate for the remediation of environmental management. So, there is an urgent need of such book which may provide fundamentals and current trends and future perspectives in the field of phytoremediation. Exchange of knowledge among the researchers working in the field of phytoremediation will be helpful through this book.

Concerning the above point of view, this book will extensively cover the various strategies of phytoremediation used in modern practices and their impact on social and environmental about them. This book will provide different aspects of phytoremediation to its reader. This book covers the fundamentals, limitations, and challenges of phytoremediation as well as how soil-plant-microbes interact in the environment. Phytoremediation of contaminated water, air, and soil due to natural processes and anthropogenic (industrial) activities are explained in this proposed book. This book explains the phytoremediation of chemical pollutants and heavy metals via different types of microbes, fungi, and various plant groups, i.e., from lower to higher plants, to improve the quality of soil, water, and air. This book covers the application of nanotechnology for phytoremediation which are emerging technology for reducing toxic pollutants. This book contains chapters related to mechanisms and molecular-level aspects of phytoremediation.

This book contains both practical and theoretical latest and broad aspects of phytoremediation. An emphasis will be made on the recent research of mechanism of phytoremediation. The chapters contain both practical and theoretical aspects and may serve as the baseline information for phytoremediation. This book will be useful for university students, researchers, and teachers especially working in field of phytoremediation.

We tried a humble attempt to reflect upon the various aspects of phytoremediation, hoping that it would be a significant addition to the already available literature. The contributors to the book having different backgrounds provide a holistic approach to the topic imbibing diverse practices and perspectives. We express our sincere gratitude to all the contributors and publishers for producing a remarkable and meaningful edited volume on an important issue.

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Cyanoremediation: An Overview

Vinod Kumar and Surbhi Kharwar

Abstract Heavy metal and organic compound pollution caused by global industrialization has significant and potentially deadly consequences for both humans and the environment. This is a widespread issue that has become a significant environmental concern due to worldwide industrialization. Various strategies have been used to rehabilitate various metal and organic compound-contaminated areas using chemical-based, physicochemical, or biological techniques. Another method of remediation is bioremediation, in which a biological system is used to remove such hazardous chemicals. This approach is a smart substitutional method compared to other conventional chemical and physicochemical methods due to some of their limitations. Today, cyanoremediation, which uses cyanobacteria, a new affordable and sustainable technology, is an emerging approach that intends to remove these pollutants from soil, water, and the atmosphere that affect the nearby ecosystems. Hence, this chapter provides a concise overview of potential cyanobacterial strains and the approach known as "cyanoremediation" for the removal and uptake of toxic heavy metals and chemical compounds. In addition, bioaccumulation and biosorption, as well as their mechanisms, are discussed. The factors influencing such technologies are also covered briefly in this chapter.

Keywords Bioremediation · Cyanoremediation · Cyanobacteria · Heavy metal · Organic compounds · Pollution · Hazardous components

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1 Introduction

The natural ecosystems worldwide have been severely degraded due to the uncontrolled use of natural resources to supply food, fuel, and fodder to an increasing human population. Human activity disturbs the natural equilibrium that is required for the survival of plants and wildlife in the atmosphere. As a result of rapid urbanization, advanced farming practices, anthropogenic developmental activities, managing public, factory, and farm waste comprising organic matter, toxic metals, and other dangerous compounds have become a big concern. Different BTEX compounds (comprising benzene, toluene, ethylbenzene and xylene), halogenated aromatic compounds, and polycyclic aromatic hydrocarbons accumulate in the environment posing health risks. Therefore, removal of these toxic pollutants has become a global problem (Lombi et al., 2001). Different methods such as physical, chemical, and biological methods have been used to treat this serious issue. Utilizing cyanobacteria to remediate pollutants is seen as less expensive, more efficient, and environmental friendly, and theycan be used as a viable alternative to traditional methods, which are known to have several drawbacks.

Cyanobacteria, or blue-green algae, are Gram-negative bacteria that evolved about 2.5–3.5 billion years ago (Hedges et al., 2001). They are found in a wide range of habitats, can flourish even in harsh environments (Castenholz & Waterbury, 1989; Schopf, 2000; Panosyan, 2015), and have shown diversity in their morphological characteristics (Klymiuk et al., 2014). The photosynthetic pigments of cyanobacteria include phycobiliproteins, carotenoids, and chlorophyll *a* (Castenholz, 2001). They are one of the essential elements of the ecosystem since they have the ability to fix atmospheric dinitrogen (Bergman et al., 1997).

Cyanobacteria are a varied group of organisms that perform both oxygenic and anoxygenic photosynthesis. They are unique in that their cells are encased in polysaccharide capsules; to put it another way, they have a lot of binding sites for organic removals such as pesticide adsorption, metal ions, agriculture, and industrial waste.

CyanoClean is a novel strategy for combating pollutants, is the use of cyanobacteria-based environmental cleanup. In the food chain, cyanobacteria is at the bottom. As a result, they consume pollutants, shielding higher-ranking species from the negative impacts of pollution. Several researches have shown that cyanobacteria are effective organisms for the remediation process. Cyanobacteria-based technologies are cost-effective and eco-friendly approaches for the removal of contaminants. According to Volesky and Naja (2007), cyanobacteria are useful in this regard since they are easily produced and genetically engineered. The utilization of cyanobacteria as a bioremediating agent was reviewed by several researchers (Pandey, 2017; Kulal et al., 2020; Kumar et al., 2020).

The present chapter describes the various remedial techniques. Furthermore, provides an insight into the bioremediation process, particularly cost-effective cyanoremediation and its mechanisms, as well as factors influencing bioremediation, and dispense a list of possible cyanobacterial species with the ability to remove hazardous contaminants. Next, we describe the advantages and challenges of cyanoremediation.

2 Heavy Metal Pollutants

New synthetic materials are being developed as a result of recent advancements in industrial, pharmaceutical, and other commodities that are discarded into the environment and contribute to human-made pollution. It includes heavy metals like arsenic, cadmium, mercury, zinc, and many more which significantly affect natural flora and fauna since they are difficult to remove from the system and can persist in the ecosystem for years (Pandey, 2017; Kulal et al., 2020). Both natural (from weathering and volcanoes) and man-made sources release heavy metals into the environment, but anthropogenic sources like smelting, mining, tanning, the use of pesticides, and automobiles are responsible for a much greater amount of the discharge than natural sources (Nriagu & Pacyna, 1988; Ahamad et al., 2020). The dumping of these heavy metals into bodies of water can damage water quality and, indirectly, affect humans via the food chain. Heavy metals occur in hydrated ionic forms in both aquatic and terrestrial environments. In addition, they can interact with colloidal substances and suspended particles in order to form compounds with ligands of inorganic and organic compounds.

Even though a few heavy metals, such as zinc, copper, and nickel, are crucial for organisms to function at low levels considering they are vital components of a variety of important enzymes and metallic proteins and play a role in the metabolic processes, they are hazardous at elevated levels. Humans who are exposed to heavy metals may experience a variety of negative side effects, including nausea, dermatitis, exhaustion, baldness, breathing problems, anxiety, migraines, diminished memory, kidney stones, arthritis, bone loss, rheumatism, cognitive tremors, and a higher blood pressure or pulse. Additionally, some heavy metals, namely cadmium, arsenic, and chromium, are known to cause cancer (Zweig et al., 1999; Costa & Klein, 2006). The impact of these elements on numerous biological processes, including biomolecules and structures, is responsible for these negative consequences. The biotoxicity of these contaminants relies on their presence, quantity, chemical composition, and period of interaction. Their mobility, bioavailability, and toxicity are influenced by the soil and water pH. Thus, this is a crucial concern for the prevention, control, and reduction of heavy metal pollution (Khatri & Tyagi, 2015; Ashraf et al., 2017).

3 Organic and Inorganic Pollutant Contamination

The negative effects of chemical pollutants on the environment are well known (Gadd, 2009). Many chemical substances, such as soap, detergent, faecal materials, dyes, phenolic chemicals, insecticides, and many more, are released from waste streams and effluents into the atmosphere (Aksu, 2005; Singh et al., 2017; Pan et al., 2021). Since they are present in trace amounts, these dye-containing effluents are exceedingly challenging to clean and are resistant to aerobic digestion and oxidizing agents. In order to eliminate pollutants at their precise origin and limit their ability to circulate, it is essential to choose the right treatment technique. Removal of harmful compounds accumulating in natural ecosystems is becoming a growing concern globally due to their negative effects on the environment (Lombi et al., 2001).

4 Remediation of Contaminants

Various approaches for the remediation of contaminants are categorized as physico-chemical and biological methods (McEldowney et al., 1993).

4.1 Physical Methods

Physical approaches involve techniques that rely solely on physical phenomena and avoid major chemical-based or biological transformations in order to remediate or manage contaminants in soil or sewage. When compared to other procedures, the physical techniques of the removal of pollutants have a relatively high application cost and low efficiency, and necessitate additional processing means that include labour-intensive operations. The size and distribution of hazardous substances serve as the primary basis for physical separation procedures. The use of thermal treatment, soil washing, soil replenishment techniques, vitrification, enclosing polluted areas (encapsulation) in impervious horizontal and vertical layers, and electroremediation are examples of physical remediation techniques.

4.1.1 Thermal Treatment

This approach involves heating sludge contaminated with toxic heavy metals and hydrocarbons to extremely high temperatures, i.e. 300–400 °C, which causes them to evaporate, complete degradation, or removed (Sharma et al., 2018).

4.1.2 Soil Washing

The primary method for washing soil involves classifying highly contaminated particles selectively, followed by phase separation of the residual suspension. Alternative methods, including leaching, flotation, or high-gradient magnetic separation, can be employed to clean fine particles.

4.1.3 Soil Replenishment Techniques

The principle behind the soil replacement approach is to replace polluted soils whole or partially in order to reduce the concentration of pollutants. With this technique, the entire polluted soil biome and its surroundings are cut off to prevent them from negatively affecting the surrounding natural and ecosystem. It has been common practice for a long time to remove harmful toxic materials and pollutants from polluted areas (Vidali, 2001). The traditional method of site cleanup entailed capping and containing the contaminated sections of the site or removing contaminated soils and transporting them to a landfill (Powrie & Robinson, 2000). The movement of contaminated soil has numerous drawbacks since it only moves the contaminants from one location to another without degrading or transforming them (Duggan, 2005). Additionally, it increases the risk of handling, transporting, and excavating hazardous materials. Also, the method is expensive and necessitates the construction of new landfills for the disposal of hazardous waste. As it required isolating contaminated sites, monitoring them, and maintaining them at their original locations for an extended period of time.

4.1.4 Vitrification

Vitrification is a technology that is useful for onsite and offsite locations for the rehabilitation of soil and waste. It is the procedure of heating (through pyrolysis or combustion at a very high temperature, i.e. 1700–2000 °C) contaminated soils to an extremely high temperature till they melt and then are quickly frozen, creating solids through glass transition. By encasing and immobilizing the contaminants, this solid creation that resembles glass, also known as a vitrified product, isolates from the environment (Bradl & Xenidis, 2005).

4.1.5 Encapsulation

Enclosing contaminated regions is called encapsulation, and it is the most commonly used practice. The majority of these methods were developed in the watertight enclosure of construction pits. The fundamental idea is to build an impermeable vertical barrier underground. Many other construction techniques have been developed, including thin walls, bored-pile cut-off walls, sheet pile walls, cut-off slurry walls primarily employing cement-bentonite–water slurries, injection walls, jet grouting curtains, and frozen barriers (Bradl & Xenidis, 2005).

4.1.6 Electroremediation

It is a promising in situ treatment technology for contaminated fine-grained soils. Based on the electrokinesis principle, electroremediation operates. This procedure concentrates the contaminants close to the electrode by using electrical currents, where they can later be retrieved. Electro-osmosis, electromigration, and electrophoresis are the three principles of electro-kinetics (Bradl & Xenidis, 2005).

4.2 Chemical Methods

Chemical remediation for the removal of contaminated water includes precipitation, ion exchange, flocculation, chemical extraction and oxidation, chemical leaching, and membrane filter processes. Whereas soil amendments (chemical fixation) are used in contaminated soils.

4.2.1 Precipitation

Precipitation is the process by which dissolved metal ions interact with other precipitants to produce insoluble compounds. By using various solid/liquid separation procedures, these solids can be separated from the supernatant liquid and sediment. During the process of precipitation, soluble ionic components transfer into a non-soluble ionic phase. It is the common technique used for efficiently removing heavy metals from polluted sources.

4.2.2 Ion Exchange

It is used for the removal of heavy metals released from industries. Heavy metal cations in the contaminated material interact with cations in the matrices to preserve the transfer of charge balance. The most widely used ion exchangers are constructed from condensation resins manufactured from phenol and formaldehyde or interlaced polystyrene and polyacrylate.

4.2.3 Flocculation

Small, colloidal solids that are not dissolved in water are grouped together to form bigger solid flocks by a process called flocculation. Sedimentation, centrifugation, or flotation is subsequently used to mechanically separate these flocks from the fluid (Bradl & Xenidis, 2005). Calcium hydroxide, iron salts such as Fe(II) and Fe(III), and aluminium salts are inorganic chemicals used during flocculation.

4.2.4 Chemical Extraction and Oxidation

In the process of chemical extraction and oxidation, various chelating agents, viz., ethylenediaminetetraacetic acid and nitrilotriacetic acid, were used to treat the sludge of heavy metal contaminants. These chelating agents have metal ion binding sites in their structure to sequester heavy metals (Xue et al., 2009).

4.2.5 Chemical Leaching

Heavy metal ions are removed after being dissolved within the leaching solvent mixture. Usually, the leaching solution has an acidic character to encourage the solubility of metal ions (pH is kept between 1.5 and 2.0). Inorganic acids like H_2SO_4, HCl, or HNO_3 are typically used to induce this acidification (Sharma et al., 2018).

4.2.6 Membrane Filter Processes

It is a method of wastewater treatment that is extensively used and is based on physical interactions between the particles and the granular media. Depending upon the pressure gradient, different membrane filters, such as microfiltration (0.5–3 bar), ultrafiltration (1–10 bar), reverse osmosis (20–100 bar), or an electrical field force (electrodialysis, which uses an electrical field), are used to filter the solution through a membrane.

4.2.7 Soil Amendments (Chemical Fixation)

Chemical fixation is the name given to the process of utilizing chemical agents to immobilize hazardous metals. The chemicals used in this procedure are known as amendments such as silica, lime, cement, and fly ash to decrease the solubility and mobility of pollutants (Sharma et al., 2018).

These various chemical methods were innovated and used to eradicate toxic pollutants, but because of their high cost, complicated technological design, and high risk of exposure to the environment and humans, they were not widely used. This method requires lots of chemicals for the removal of toxic substances. Thus, bioremediation, i.e. using biological systems for cleaning up polluted sites, appears to be a better alternative option (Matsunaga et al., 1999; Ribeiro et al., 2008).

4.3 Biological Methods

A biological method i.e., bioremediation is a pollution control strategy that uses biological processes to accelerate the breakdown, transformation, eradication, immobilization, or detoxification of toxic compounds into less hazardous forms. It is an alternative method to conventional remediation methods; as well as a natural process occurring in the environment to clean up the pollutant effectively (El-Kassas & Mohamed, 2014). In the bioremediation process, different microorganisms were used, i.e. eubacteria, cyanobacteria, algae, yeasts, fungi, and plants. It is environmentally friendly and cost-efficient (Leong & Chang, 2020).

Metals with unknown physiological or metabolic functions can also be sequestered and accumulated by microbial cells in addition to those that are necessary for their growth and metabolism. Biosorption, bioaccumulation, and chemical transformation are the fundamental processes of heavy metal remediation performed by the microorganisms. The mechanism by which some microbes naturally attach, concentrate, or impede heavy metal ions on the surface of the cell, particularly on the cell wall, is known as biosorption. Both dead (inactive) and living (active) cells, or biomass, endure this process. Cell wall and exopolysaccharides contribute to the biosorption of metal due to the presence of negatively charged groups for example carboxyl, sulphhydryl, hydroxyl, carbonyl, amino, thiol, sulphonate, and phosphate, which can interact with the metals and radionuclide species (Vieira and Volesky, 2000; Gadd, 2009; Wang & Chen, 2009).

5 Bioremediation: An Eco-Friendly Approach

It was necessary to create remediation strategies for either decreasing or eliminating heavy metal pollution that were cheap and environmentally safe (Delneuville et al., 2019). Conventional techniques based on physical and chemical procedures include reversible osmosis, ion exchange, separation of membranes, oxidation of chemicals, and chemical reduction. These technologies are expensive, technologically complex, and unfriendly to the environment. When heavy metals are found in very small amounts, the efficacy of these conventional approaches is compromised (Volesky, 1994; Kapoor & Viraraghavan, 1995). Bioremediation is a scientifically straightforward, cheap, efficient, and sustainable alternative to conventional treatments. Due to this, the process is gaining importance nowadays.

The findings claim that biological material has the potential to remove toxic substances and solve environmental problems. The cyanobacterial biomass can be used for different purposes, such as biofertilizers, biofuel, and other biotechnological purposes, and as an agent for remediation processes (Fig. 1).

“Bioremediation“combines “bio” and “remediation”, where “bio” stands for “biological” and “remediation“for “to remedy”. The phrase “bioremediation“refers to the process of removing hazardous material from a contaminated environment utilizing plants and microbes, either native to the contaminated location or brought from outside. The toxins or pollutants are removed (either completely or partially) from the surrounding atmosphere or transformed into compounds that are less harmful depending on their chemical composition, characteristics, and the metabolic capabilities or activities of the organisms involved.

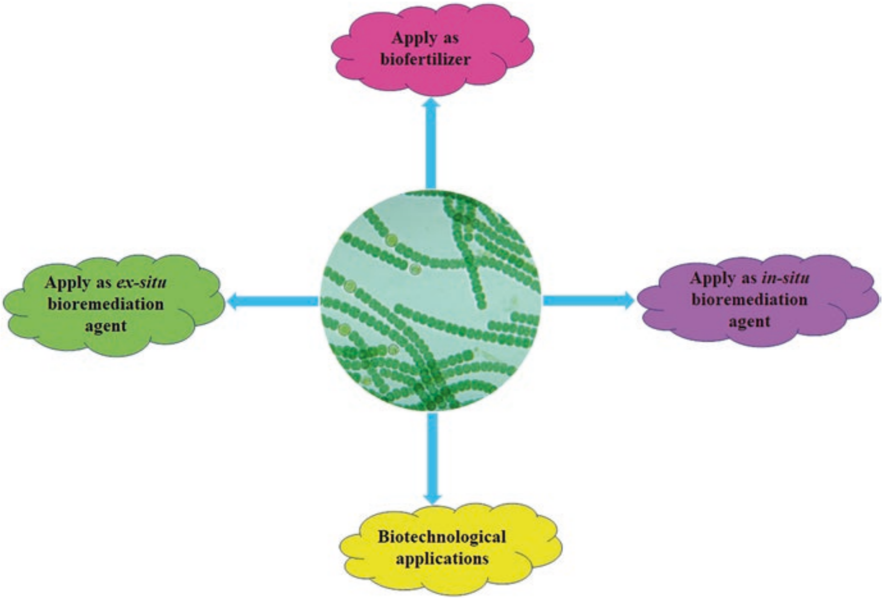

Fig. 1 Model representing the advantages of cyanobacteria in the removal of pollutants

Bioremediation is a technological procedure that removes chemical fertilizers, pesticides, heavy metals, or other toxic substances from fields as well as toxic waste effluents that have been discharged by companies. According to several researchers, such removal procedures can be accomplished by either naturally occurring or genetically engineered suitable plants or microbes (Ripp et al., 2000; Sayler & Ripp, 2000; Seidel et al., 2004). The primary aim of bioremediation is to remove toxins from polluted sites or industrial discharges using biological entities (Subramanian & Uma, 1999; Vanhoudt et al., 2018; Singh et al., 2020). Intrinsic bioremediation and engineered bioremediation are two subcategories of bioremediation technology.

5.1 Intrinsic Bioremediation

Intrinsic bioremediation, which is better suited for remediating soil with low levels of pollutants, is commonly defined as the destruction of arsenic by naturally occurring microorganisms without human involvement.

5.2 *Engineered Bioremediation*

Engineered bioremediation frequently depends on human intervention to improve the environmental conditions that will encourage the growth and activity of microorganisms. Therefore, the use of engineered bioremediation methods is more advantageous for heavily contaminated areas.

Bioremediation can be categorized into two basic methods, i.e. in situ and ex situ bioremediation. The term "in situ technique" refers to the use of methods to restore polluted soil and water on the spot with the least amount of disruption. In situ bioremediation techniques are one of the most cost-effective, least detrimental to the system, and most reliable methods for removing hazardous waste from polluted areas (Ellis et al., 2000). They also avoid the expensive excavation and transfer of toxins. In situ bioremediation of groundwater and soil contaminated with pollutants can be accomplished using indigenous microbes. Whereas ex situ approaches refer to the use of methods on contaminated soil and water that have been excavated (for soil) or pumped (for water) from the contaminated site. These methods entail the excavation of toxic soil from polluted locations and its subsequent action for bioremediation in a different place. Whilst ex situ bioremediation is expensive, it offers benefits compared to in situ, takes less time, and provides greater assurance regarding the homogeneity of the treatment because it can homogenize, screen, and mix soil continuously (Fig. 1).

Bioremediation is a broad term that has two components: **phytoremediation**, used to describe the elimination of hazardous chemicals by higher plants, and **microbial remediation**, where microbial organisms are used to clean the environment. Several reports demonstrated that prokaryotic (bacteria and cyanobacteria) and eukaryotic microorganisms like microalgae and fungi have the ability to remediate pollutants (Brady & Duncan, 1994; Vieira and Volesky, 2000; De Philippis et al., 2003; Wang & Chen, 2006). Another term, i.e. phycoremediation, is used for the removal of toxic substances by algae, while cyanoremediation means the process of removing toxic substances by using cyanobacterial strains (Dutta et al., 2022; Mona et al., 2020; Zanganeh et al., 2022). Microbial bioremediation, i.e. cyanoremediation, has received more attention than phytoremediation because of the widespread dispersion of microorganisms in the environment, their tremendous capacity to adapt to changing environmental conditions, their rapid growth rate, and their versatile metabolic processes (Kumar et al., 2020).

6 Cyanoremediation

The use of cyanobacteria in the removal of pollutants called cyanoremediation (CyanoClean) has been recognized as a less expensive, more efficient, and environmental friendly alternative to the traditional physico-chemical remediation approaches. Figure 2 depicts the usage of cyanobacteria in the treatment of wastewater from diverse fields.

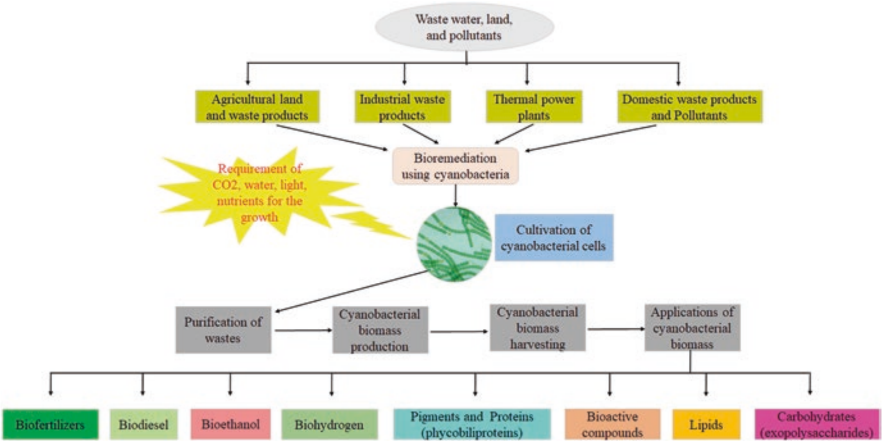

Fig. 2 Model depicting the bioremediation (by utilization of cyanobacteria) of wastewater, land, and pollutants released from several sectors

Cyanobacteria colonize and inhabit a variety of habitats due to their remarkable resilience and efficient defence mechanisms against numerous abiotic stresses (Turner & Robinson, 1995; Potts, 1999). Numerous cyanobacterial species eliminate heavy metals via different mechanisms, i.e. forming metal-sequestering compounds, such as exopolysaccharides and intracellular polyphosphate bodies, and metal-binding proteins, such as metallothionein and phytochelatines. Cyanobacterial removal of heavy metals can be done by biosorption and bioaccumulation. Despite this, cyanobacteria produce certain enzymes that can break down oils, herbicides, and pesticides. These enzymes are produced by different cyanobacterial species such as isocitrate lyase, enol-pyruvyl-shikimate-3-phosphate (EPSP) synthase, alkaline phosphatase, NADP reductase, organophosphorus hydrolase, glutathione S-transferase, polyphenol oxidase, glutamine synthetase, phytoene desaturase, respectively, phorate, glyphosate, chlorpyrifos, methyl parathion, organophosphates, bentazon, chlorpyrifos, carbofuran, and norflurazon (Sudharsanam et al., 2019). Table 1 provides the merits of cyanobacteria over other microbes which are used in the bioremediation process.

7 Mechanism of Cyanoremediation

The term “bioaccumulation” describes internalization or intracellular uptake due to the efficient uptake system, which facilitates intracellular transport as well as the accumulation of different heavy metals from the adjacent atmosphere (Nies, 1999). In contrast to biosorption, bioaccumulation (an active process) occurs exclusively in live cells. In the chemical transformation process, a harmful heavy metal undergoes chemical transformation when the microorganisms‘metabolic or enzymatic activity

Table 1 Advantages of cyanobacteria over other microbes used in the bioremediation process

S. No.	Characteristics	Cyanobacteria	Other microbes
1.	Mode of nutrition	Photoautotrophic	Heterotrophic
2.	Cultivation/ Maintenance	Limited maintenance	Regular maintenance
3.	Maintenance cost	Low maintenance cost	High maintenance cost
4.	Bioremediating agent	Apply as both in situ and ex situ	Only apply as ex situ (in most of the cases)
5.	Correlation with environment	Environmentally friendly	Sometimes toxic in nature due to the production of toxic molecules
6.	Biomass separation	Biomass of cyanobacteria are easily separated	Typical separation of biomass

changes it into a harmless or less hazardous. According to the researchers, methylation and demethylation are the most common processes involved in the microbial alteration of metals (Chirwa & Wang, 1997; Barkay et al., 2003; Lloyd, 2003). Algal biomass is most commonly employed for the remediation process because of its wide availability and exceptional enactment (Al-Homaidan et al., 2014). Thus, the potentially green method of bioremediation is the use of promising cyanobacterial strains for the detoxification of pollutants. Heavy metals can be eliminated in two approaches, i.e. physical adsorption (also called biosorption) and absorption (also known as chemisorption or bioaccumulation) (Bloch & Ghosh, 2022) (Fig. 3).

Biosorption happens on the cell surface, whereas bioaccumulation happens within the cell. Physical adsorption was performed using live algal cells, and it is a rapid procedure with a reversible response on the cell surface, whereas bioaccumulation is an intensive procedure accomplished using dead and live cells (Pandey et al., 2022; Aksu & Kutsal, 1990). These methods extract metal-saturated algae from the substrate, leading to excellent quality, usable wastewater (Sari and Tuzen, 2008).

7.1 *Mechanisms of Biosorption*

Biosorption is described as the elimination of potentially dangerous compounds using various approaches that can be metabolically dependent or metabolically independent (Veglio' & Beolchini, 1997). Later scientists classified bioaccumulation and biosorption as metabolism-dependent and metabolism-independent processes, respectively (Volesky, 2007; Chojnacka, 2010). In contrast to bioaccumulation, it is an inactive procedure that proceeds more quickly (rapid kinetics since the cells are not impacted by the concentration of pollutants). Another benefit of biosorption is the use of cells for numerous desorption and adsorption cycles, which extends their lifespan and increases their economic worth.

Adsorption, complexation, ion exchange, coordination, chelation, and surface precipitation are the various mechanisms commonly associated with the biosorption

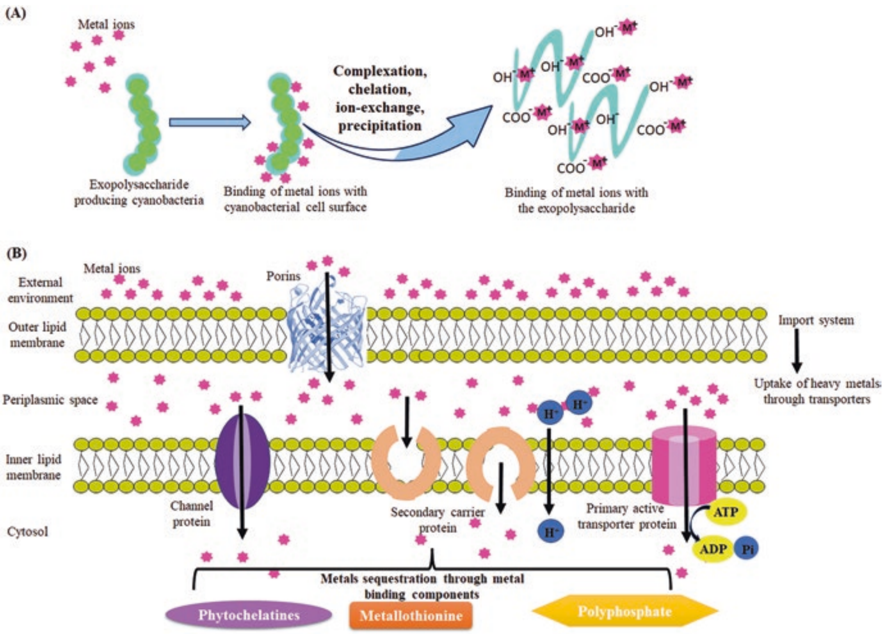

Fig. 3 (**a**) Model showing the biosorption of heavy metals by exopolysaccharides of cyanobacteria. (**b**) Diagram representing bioaccumulation of heavy metals using different transporters inside the cyanobacterial cell

process (Abd El Hameed et al., 2015; Bhatt et al., 2022). These diverse processes have different outputs in terms of both quality and quantity depending on the microbes used, where the biomass came from, and how it was prepared (Volesky & Holan, 1995).

The most significant biosorption mechanism, according to Vijayaraghavan and Raja (2015), is ion exchange. The author also noted that it happens as a result of various functional groups present on the surface of microbes (Vijayaraghavan & Raja, 2015). The term "physical adsorption" refers to adsorption accomplished by Van der Waals forces. Furthermore, Kuyucak and Volesky (1988) revealed that metal ion sorption by non-living cells is because of an electrostatic reaction between metal ions along with cell walls, whereas copper biosorption occurs with electrostatic interactions in the case of *Chlorella* (Aksu & Kutsal, 1991). The mechanism of complexation involves active groups on the cell surface and metal ions (Treen-Sears et al., 1984). Macrophytes basically do the biosorption of hazardous substances by an ion-change process (Verma et al., 2008). The presence of functional active groups, such as the carboxyl groups of alginic acid and the carboxyl and sulphate of fucoidan, aided ion exchange in the case of marine algae (Treen-Sears et al., 1984).

Bioaccumulation in cyanobacteria: Bioaccumulation is considered a paramount mechanism for heavy metal sequestration or elimination in case of cyanobacteria

(Bhatt et al., 2022). The cyanobacterial cell wall possesses negatively charged groups that are involved in binding with metal ions (De Philippis and Micheletti, 2017; Mota et al., 2022). As a result, metal ions can pass via active transporters and carriers before entering cells, where they are broken down into less harmful forms and further stored.

7.2 Mechanisms of Bioaccumulation

Bioaccumulation refers to the process by which an anthropogenic chemical is successfully taken up by organisms from their environment and distributed within their protoplasm. The process of bioaccumulation is reported in few species of algae and cyanobacteria (Lengke et al., 2006; Doshi et al., 2008; Sodaeizade et al., 2020). In cyanobacteria, the mechanisms of bioaccumulation include oxidation, reduction, dissolution, leaching, and sorption. Phosphate and peptide moieties help in the uptake of heavy metals. Bioaccumulation includes all methods, i.e. adsorption, passive diffusion, and special transport. Blanco et al. (2019) stated that other parameters, such as the abundance of xenobiotics and the lipophilic properties of the pollutant, influence the accumulation rate. The lipophilic characteristic of xenobiotics promotes bioaccumulation. Bioaccumulation of xenobiotics occurs through passive diffusion and adsorption. Another mechanism of xenobiotic uptake is also reported, i.e. facilitated transport, which is governed by energy. Recently, Zhu et al. (2020) demonstrated that adsorption is one of the most frequent surface phenomena of xenobiotic absorption occurring in the aqueous medium. Covalent and electrostatic forces are involved in direct adsorption. Particularly, adsorption represents the initial stage of bioaccumulation.

Other related elements, such as actinides, lanthanides, and metalloids, as well as a number of radioisotopes of these compounds, have been researched in addition to metals. Furthermore, particles and colloids, together with organometal (loid) and organic compounds, have recently received attention (Aksu, 2005).

8 Factors Affecting Cyanoremediation

Several factors influence the functioning of biological decontamination solutions (Fig. 4).

These are the initial concentration of toxic substances, growth conditions (such as nutrients, light, and temperature), organisms (namely species, strains, biovars, and biomass), physicochemical traits such as pH, cations (e.g. K^+, Na^+, and Ca^{2+}), and/or anions (e.g. PO_4^{3-} and CO_3^{2-}), and modification of biosorbents (Gadd, 2009; Rai, 2009; Fomina & Gadd, 2014; Mani & Kumar, 2014; Zeraatkar et al., 2016; Bouzikri et al., 2020; Coelho et al., 2020). A change or adjustment in these conditions could result in a significant impact on the remediation potential. The following factors are explained briefly in the different sections.

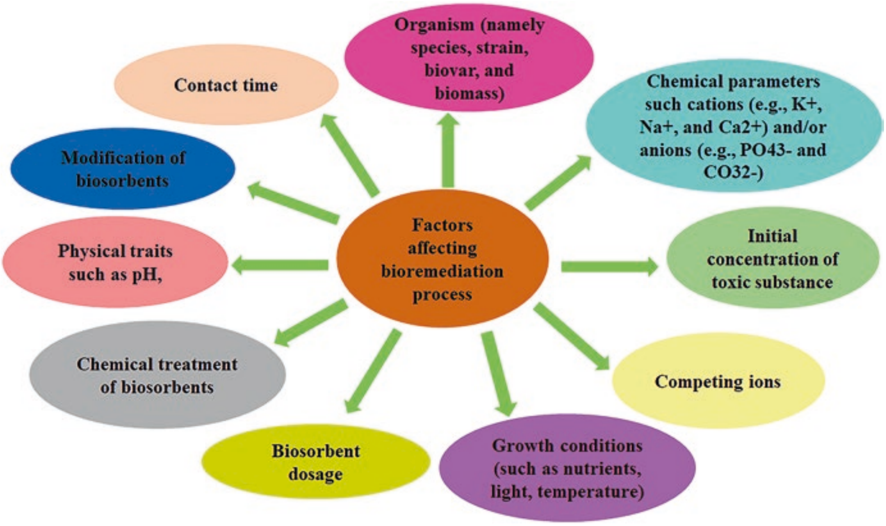

Fig. 4 Factors influencing the bioremediation process

8.1 pH

Vanhoudt and his colleagues recognized pH as the most significant factor for radionuclide remediation from polluted water (Vanhoudt et al., 2018), whereas Mashkani and Ghazvini (2009) have shown that the detoxification of heavy metals and radionuclides is greatly influenced by pH because it influences the surface charge of the biosorbents and determines the species of the contaminants in the solution. Another possible explanation is hydroxyl ions and positively charged heavy metal ions fight for binding sites (Bulgariu & Bulgariu, 2012; Tavana et al., 2020).

Similarly, Sun et al. (2014) found that at pH 6.8, there is maximal removal efficiency for the Sb sorption by *Microcystis* as compared to pH 2.8. Percentage removal of 134Cs and 85Sr by the cyanobacterial species was increased with high pH, but not in the case of 241Am. 241Am showed the opposite trend in response to pH, as reported by Pohl and Schimmack (2006).

8.2 Competing Ions

Competition for binding sites on the microbial cell surface during the biosorption process may also interfere with the active process of bioaccumulation when identical membrane transporters are used for the uptake of metals. Aquatic nutrients (for instance, Ca^{2+}, K^{+}, Mn^{2+}, Fe^{2+}, and so on) or contaminants found within the mixture, as is often the case in actual contamination circumstances, can act as such ionized competitors. Compared to metal ions that have lower starting concentrations, metal ions with higher starting concentrations have a better chance of reaching the active sites and as a consequence have a greater probability of adsorption (Aksu & Dönmez, 2006).

The presence of co-contaminants acts as a competitor for the uptake of elements by cyanobacteria. Similar evidence of the adverse effects of Zn contamination and their removal was found for the dead biomass of *Lyngbya taylorii* (Klimmek et al., 2001). Zinc intake declined by 3–5 times in equimolar solutions of Cd^{2+}, Pb^{2+}, Ni^{2+}, and Zn^{2+} in comparison with Zn^{2+} intake in a zinc-only solution. Likewise, the lack of Pb^{2+} was observed whether or not the *Lyngbya taylorii* sorbent was subjected to chemical treatment (which under all circumstances related very well and quickly to the *Lyngbya taylorii* sorbent) led to significantly enhanced Zn^{2+} removal (Klimmek et al., 2001). In bi- and tri-metal studies, Pradhan et al. showed that Ni^{2+} and Cr^{6+} had no influence on the Fe^{3+} adsorption of live *Microcystis*, but had a significant impact on Cr^{6+} adsorption (Pradhan et al., 2007).

8.3 Temperature

An increase or decrease in the temperature affects the remediation process. Adsorption of heavy metals declines as temperature rises, as reported by Bulgariu and Bulgariu (2012).

8.4 Contact Time

Heavy metal absorption involves several phases, and over 90% of adsorption takes place in just a couple of minutes upon contact a period of time shortly after that a state of equilibrium is accomplished. In the first phase, fast adsorption followed by uptake by the microbial cells occurred (Bulgariu & Bulgariu, 2012).

8.5 Initial Metal Concentration

A rise in the initial metal concentration affects the remediation proportion of harmful compounds due to the total number of occupied active sites increasing with metal quantity, which leads to a lack of metal ions binding sites at higher levels (Tavana et al., 2020).

8.6 Biosorbent Dosage

Up to a certain point, increasing biosorbent concentration improves heavy metal extraction; however, adsorption then declines as a result of biosorbent particle consolidation blocking active sites (Gupta & Rastogi, 2008).

8.7 Modification of Biosorbents

Several researchers have reported that the presence of oxygen on the biosorbent surface and changes in their chemical structure play a major role in biosorption. Chemical modification in the functional groups will improve remediation (Coelho et al., 2020; Bouzikri et al., 2020).

8.8 Chemical Treatment of Biosorbent

A physical or chemical change in the biomass of photosynthetic organisms elevates the accessibility of ion-binding active groups on the sorbent's surface and subsequently increases the sorbent's capacity to bind elements. Pohl and Schimmack reported that, through phosphorylation, the biosorption ability of sorbents made from diverse algal and cyanobacterial species was improved for several elements (Pohl & Schimmack, 2006). The dead biomass of the cyanobacterial cells of *Oscillatoria geminata* and *Nostoc carneum* was heated (170 °C) using urea and phosphoric acid, after which the biomass was washed, dried, and sieved, and the increased biosorption capacity was assessed.

9 Advantages of Cyanoremediation

Biological remediation, and most importantly, cyanoremediation, has the following advantages: cyanobacteria have rapid kinetics for the detoxification of pollutants and heavy metals. In addition, it is utilized as a naturally abundant, renewable biological material. Furthermore, because of their photoautotrophic nature, it is likely that cyanobacterial species can be grown and maintained at a lower cost than other microbes, and also certain species can fix dinitrogen from the environment. The total quantity of solar energy, organic matter, and inorganic substances required to promote maximal cyanobacterial growth, on the other hand, varies with species. Furthermore, cyanoremediation processes yield remarkably little sludge and greatly decrease the economic and environmental costs of waste disposal in comparison with typical methods. The produced biomass of cyanobacteria which is utilized in the remediation process can further be used for making a variety of biomass-based goods with multiple uses, such as forms of energy production, for example biodiesel, biomethane, ethanol, hydrogen, and so on (Encarnação et al., 2023; Gupta et al., 2016). These systems are also useful for performing cycles of adsorption and desorption and/or for recovering biomass contaminated with metals that can be discarded for later valorization.

Due to the cosmopolitan behaviour of cyanobacterial species, they degrade pollutants into simple, non-toxic, useable inorganic products for example carbon dioxide and water, which are further allocated in the biogeochemical cycle (Pandey et al., 2005; Yadav et al., 2021). Since cyanoremediation involves different cyanobacterial species for the removal of toxic substances, it requires a very small amount of money, making it a highly cost-effective technique that saves our ecosystem from hazardous compounds as compared to physicochemical remediation methods.

Carbon dioxide (CO_2) is of serious environmental concern, and the cyanobacteria (used in cyanoremediation) have great potential to perform CO_2 fixation to reduce the carbon footprint, as they possess a carbon-concentrating mechanism to concentrate the carbon dioxide. They perform higher photosynthetic activity in comparison to the higher land plants. The characteristics of cyanobacteria are that they are found in different types of aquatic conditions, including fresh and marine waters. Halophilic means they tolerate various extreme environments (Gehlot et al., 2022); thus, they can be used at different industrial effluent sites to combat the sinking of CO_2, along with nitrogen oxide (NOx) and sulphur oxide (SOx) (Rau et al., 2007; Jansson & Northen, 2010). Table 2 provides a catalogue of cyanobacteria involved in the remediation of pollutants.

10 Challenges of Cyanoremediation

Although cyanoremediation has several pros, still using cyanobacteria for the removal of toxic and hazardous components has some cons. Metal removal techniques using cyanobacteria are slower than those using conventional chemicals (Becker, 1983; El-Bestawy, 2008; Palaniswamy & Veluchamy, 2017). Additionally, some of the cyanobacterial species for example *Microcystis aeruginosa*, *Nodularia* sp., *Anabaena circinalis*, *Planktothrix* sp., and *Cylindrospermopsis raciborskii* are poisonous, which means they produce several toxins and can endanger the local aquatic ecology (Falconer & Humpage, 2005; Doshi et al., 2009). Hence, before using cyanobacteria (which produces toxins) in the bioremediation process, it is necessary to make them non-toxic.

Table 2 Contaminants (heavy metals, oil pollutants, pesticides, and many more) removed from some of the cyanobacterial species

S. No.	Cyanobacterial strains involved in the remediation process	Contaminants/Pollutants	References
1.	*Anabaena subcylindrica, Nostoc muscorum*	Mn	El-Sheekh et al. (2005)
2.	*Anabaena subcylindrica, Nostoc muscorum*	Pb	Raungsomboon et al. (2006)
3.	*Agmenellum quadruplicatum*	Naphthalene	Cerniglia et al. (1979)
4.	*Anabaena cylindrica*	Cu, Ni	Tien et al. (2005); Corder and Reeves (1994); Campbell and Smith (1986)
5.	*Anabaena flos-aquae*	Ni	Corder and Reeves (1994)
6.	*Anabaena oryzae*	Zn, Cu	El-Bestawy (2008)
7.	*Anabaena spiroides*	Cu	Tien et al. (2005)
8.	*Anabaena variabilis*	Cr, Zn, Cu	Garnham and Green (1995); El-Bestawy (2008)
9.	*Anabaena subcylindrica, Nostoc muscorum*	Cu	El-Sheekh et al. (2005)
10.	*Anacystis nidulans*	Ni, Zn, Cd	Singh and Yadava (1985); Awasthi and Rai (2004)
11.	*Aphanothece flocculosa*	Hg	Cain et al. (2008)
12.	*Aphanothece halophytica*	Hg, As, Cd	Laloknam et al. (2009)
13.	*Aphanothece sacrum*	Nd	Okajima et al. (2010)
14.	*Arthrospira platensis*	Pb (II)	Duda-chodak et al. (2013)
15.	*Aulosira fertilissima*	Pb, Cu, Cd, Zn, Ni	Singh et al. (2007)
16.	Blue-green marine algae	Ni (II)	Ramadoss and Subramaniam (2019)
17.	*Calothrix sp.*	Cu^{2+}, Cd^{2+}, and Pb^{2+}	Yee et al. (2004)
18.	*Chlorophyta hydrodictyon*	MB	Muzarabani et al. (2015)
19.	*Chroococcus multicoloratus* and *Oscillatoria trichoides*	Pb^{2+}	Miranda et al. (2013)
20.	*Chroococcus paris*	Cd, Cu, Zn	Les and Walker (1984)
21.	*Chroococcus* sp., *Nostoc calcicole*	Cr	Anjana et al. (2007)
22.	Cyanobacteria	B, Mo, Se, Zn	Sedykh et al. (2005)
23.	Cyanobacteria	Polycyclic aromatic hydrocarbons	Cerniglia (1992)

(continued)

Table 2 (continued)

S. No.	Cyanobacterial strains involved in the remediation process	Contaminants/Pollutants	References
24.	*Cyanobacterium metallothionein*	Cd	Yang et al. (2012, 2015)
25.	*Cyanospira capsulate* and *Nostoc PCC 7936*	Cu (II)	De Philippis et al. (2003)
26.	*Cyanospira capsulata*	Cu, Cr, Zn, Ni	De Philippis et al. (2003); Paperi et al. (2006); De Philippis et al. (2007); Micheletti et al. (2008)
27.	*Cyanospora capsulata* and *Nostoc* PCC 7936	Cu (II)	De Philippis et al. (2003)
28.	*Cyanothece* 16Som 2	Cu (II), Cr (III), and Ni (II)	Micheletti et al. (2008)
29.	*Cyanothece* and *Nostoc* sp.	Cu	Micheletti et al. (2008)
30.	*Cyanothece* strain ET5 and 16Som2	Cu, Cr	Micheletti et al. (2008)
31.	Dried biomass *Lyngbya majuscule*	Cu (II)	Kushwaha and Dutta (2017)
32.	*Gloeocapsa lithophora, Cyanothece* sp.	Ba	Cam et al. (2016)
33.	*Gloeocapsa*	Pb	Raungsomboon et al. (2008)
34.	*Gloeocapsa gelatinosa*	Pb	Raungsomboon et al. (2006)
35.	*Gloeocapsa* sp.	Zn, Cd, Pb, and Cu	Pokrovsky et al. (2008, 2013)
36.	*Gloeomargarita lithophora, Cyanothece* sp.	Sr	Cam et al. (2016)
37.	Live and dead *Spirulina* sp.	As (V)	Doshi et al. (2009)
38.	*Lyngbya major*	^{199}Tl, Hg, Pb	Nayak et al. (2002)
39.	*Lyngbya putealis* HH-15	Cr (VI)	Kiran and Kaushik (2008)
40.	*Lyngbya wollei*	Cu	Bishop and Rodgers Jr (2012)
41.	*Microcystis aeruginosa*	Cd and Pb	Rzymski et al. (2014)
42.	*Microcystis aeruginosa*	Cu^{2+}, Cd^{2+}, and Ag^{+}	Tao et al. (2014)
43.	*Microcystis aeruginosa*	Tetracycline	Pan et al. (2021)
44.	*Microcystis aeruginosa*	Cu	Tien et al. (2005)
45.	*Microcystis aeruginosa*	Phenanthrene	Bai et al. (2016)
46.	*Microcystis aeruginosa*	U	Li et al. (2004)
47.	*Microcystis* sp.	Cu^{2+} and Cd^{2+}	Tao et al. (2013)

(continued)

Table 2 (continued)

S. No.	Cyanobacterial strains involved in the remediation process	Contaminants/Pollutants	References
48.	*Microcystis* sp.	Ni	Rai et al. (1998)
49.	*Microcystis* sp.	Rhodamine B	He et al. (2014)
50.	*Microspora* sp.	MB	Maurya et al. (2014)
51.	*Nostoc calcicola, Chroococcus* sp.	Cr	Anjana et al. (2007)
52.	*Nostoc linckia, Nostoc rivularis*	Zn	El-Enany and Issa (2000)
53.	*Nostoc muscorum*	Cr (VI)	Gupta and Rastogi (2008)
54.	*Nostoc muscorum* and *Anabaena subcylindrical*	Cu^{2+}, Pb^{2+}, Co^{2+}, and Mn^{2+}	El-Sheekh et al. (2005)
55.	*Nostoc muscorum, Anabaena subcylindrica*	Co	El-Sheekh et al. (2005)
56.	*Nostoc muscorum, Anabaena subcylindrica*	Cu	El-Sheekh et al. (2005)
57.	*Nostoc muscorum, Anabaena subcylindrica*	Mn	El-Sheekh et al. (2005)
58.	*Nostoc muscorum, Anabaena subcylindrica,* and *Gloeocapsa* sp.	Pb	El-Sheekh et al. (2005); Raungsomboon et al. (2006)
59.	*Nostoc rivularis, Nostoc linckia*	Zn	El-Enany and Issa (2000)
60.	*Nostoc rivularis, Nostoc, linckia, Tolypothrix tenuis*	Cd	Inthorn et al. (1996); El-Enany and Issa (2000)
61.	*Nostoc calcicole*	Cu	Verma and Singh (1990)
62.	*Nostoc calcicola*	Cu, Hg	Singh et al. (1989, 1992); Pandey et al. (1992); Pandey and Singh (1993)
63.	*Nostoc calcicola* HH-12 and *Chroococcus* sp. HH-11	Cr (VI)	Anjana et al., 2007
64.	*Nostoc linckia*	Zn	El-Enany and Issa (2000)
65.	*Nostoc linckia, Nostoc rivularis, Tolypothrix tenuis,* and *Microcystis*	Cd	Inthorn et al. (1996); El-Enany and Issa (2000); Rai et al. (1998)
66.	*Nostoc minutum* and *Anabaena spiroides*	Pb, Cd, and Ni	Al-Sherif et al. (2015)
67.	*Nostoc muscorum*	Cu, Zn, Pb, Cd	Hazarika et al. (2015); Goswami et al. (2015)
68.	*Nostoc muscorum*	Zn^{2+}	Diengdoh et al. (2017)

(continued)

Table 2 (continued)

S. No.	Cyanobacterial strains involved in the remediation process	Contaminants/Pollutants	References
69.	*Nostoc muscorum, Anabaena subcylindrica*	Co	El-Sheekh et al. (2005)
70.	*Nostoc* PCC 7936	Cu, Cr, Zn, Ni	Micheletti et al. (2008), De Philippis et al. (2007); De Philippis et al. (2003)
71.	*Nostoc punctiforme* A. S/S4 and *Chroococcidiopsis thermalis* S.M/S9	^{238}U, Cd, and ^{226}Ra	Heidari et al. (2018)
72.	*Nostoc rivularis*	Cd	El-Enany and Issa (2000)
73.	*Nostoc* sp.	Cr	Warjri and Syiem (2018)
74.	*Oscillatoria laete-virens* (Crouan and Crouan) Gomont and *Oscillatoria trichoides*	Cr^{6+} and Pb^{2+}	Miranda et al. (2012a, b)
75.	*Oscillatoria homogenea*	^{90}Sr	Dabbagh et al. (2007)
76.	*Oscillatoria laete-virens*	Cr (VI) and Ni (II)	Das (2012)
77.	*Oscillatoria laete-virens*	Cr, Pb	Miranda et al. (2012a, b)
78.	*Oscillatoria salina* Biswas, *Plectonema terebrans* Bornet ex Flahault and *Aphanocapsa* sp.	Aliphatics (hexadecane), waxes and bitumen and aromatics (anthracene and phenantherene)	Raghukumar et al. (2001)
79.	*Oscillatoria* sp.	Pb, Cd, Cu, Zn, Co, Cr, Fe, and Mn	Bender et al. (1989), (1991a, b)
80.	*Oscillatoria* sp.	Paraquat and 2,4-dichlorophenoxyacetic acid pesticides	Kumar, et al. (2010b)
81.	*Oscillatoria* sp. H1	Cd (II)	Katırcıoğlu et al. (2008)
82.	Oscillatoria sp. NTMS01	Pb, Cr	Kumar et al. (2011); Rajeshwari et al. (2012)
83.	*Oscillatoria* sp., *Nostoc* sp., *Anabaena* sp., *Gloeocapsa* sp., *Plectonema* sp., and *Gloeothece* sp.	Cr (VI)	Gahlout et al. (2017)
84.	*Oscillatoria* sp., *Phormidium* sp., *Lyngbya* sp., *Aulosira* sp., and *Scytonema* sp.	Cu (II), Cd (II), and Pb (II)	Kumar, (2010a)
85.	*Oscillatoria trichoides*	Cr	Miranda,(2012a)
86.	*Phormidium* sp.	Pb, Cu, Cd, Zn, Ni	Wang et al. (1998)

(continued)