Review

Microorganism remediation strategies towards heavy metals

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HIGHLIGHTS

- Heavy metal detoxification pathways of microorganisms have been summarized.
- Heavy metal remediation mechanisms of microorganisms have been included.
- Interactions between remediation mechanisms and detoxification pathways were discussed.
- The next-generation of bioremediation technologies has been put forward.

GRAPHICAL ABSTRACT

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ABSTRACT

Heavy metal pollution, because of its high toxicity, non-biodegradability and biological enrichment, has seriously threatened the health of human beings and the stability of ecological system. The immobilization, removal and detoxification of active heavy metal ions in natural environment can be achieved through microbial activities. Because of its outstanding advantages including high efficiency, low cost and environment friendly, the development of high-efficiency biological techniques to clean up toxic metal wastes have already drawn scientists' great attention. After millions of years of evolution, some microorganisms are resistant to heavy metal ions and able to remediate heavy metal pollution. However, the relationship of microbial resistance system and their remediation ability towards heavy metal ions is still unclear. To uncover the underneath, we summarized heavy metal bioremediation technologies as well as their detoxification pathways in this review, which will contribute to find their interconnections and develop more efficient bioremediation technologies. Additionally, the future potential of gene-editing associated and advanced material associated multi-functional bioremediation technologies have been put forward in this review.

1. Introduction

Nowadays, heavy metal pollution caused by mining, steel production, and electroplating has induced an adverse impact on the environment, which threatens the health of human beings and the

stability of ecosystem [1]. Heavy metal ions can be accumulated through food chain, which is believed to be a risk for human beings even at trace level [2]. Additionally, heavy metal ions can affect cellular organelles, components, and induce oxidative stress. For instance, arsenic can induce DNA hypomethylation and further facilitates aberrant

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gene expression [3]; chromium can induce DNA damage and oxidative stress in Sprague–Dawley rats and in human liver carcinoma cells [4]; copper has been reported to take part in the oncogenic BRAF signaling which is related to various cancers [5]. As a consequence, numerous diseases such as Menkes disease, Alzheimer's disease and cancers can be induced by the excessive intake of heavy metal ions [6]. Therefore, heavy metal pollution has already become one of the most serious environmental problems and the remediation of active heavy metal ions is of great importance.

Recently, a series of technologies such as chemical precipitation, ion-exchange and membrane filtration have been developed to remove heavy metal ions from polluted area, which focus on reducing metal bioavailability by transforming the heavy metal to the inactive state [7–9]. Among them, chemical precipitation method is simple, inexpensive and effective, which has become one of the most widely used methods for heavy metal treatment [7]. However, chemical precipitation method will generate low-density sludge and induce secondary pollution, which has many limitations and difficulties to clean up trace heavy metal pollution in large area. Ion-exchange resin for heavy metal treatment has high removal efficiency, high treatment capacity, and fast kinetics [8]. However, most ion-exchange techniques need to be used at acidic environment which limits their application. Membrane filtration technologies can remove heavy metal ions with high efficiency, but the production of membrane material is usually very complicated [10]. Traditional heavy metal remediation methods have many limitations including production of toxic chemical sludge and not eco-friendly. Therefore, simple and low-cost remediation method is urgently needed.

Nowadays, bioremediation technologies based on microorganisms have attracted scientists' great interest because of their outstanding advantages including high efficiency, low-cost and environment-friendly, especially at low metal concentrations. Compared with plants and animals, microorganisms can resist environment stress through rapid mutation and evolution. Toxic heavy metal ions in active form influence the diversity and metabolic activity of microorganisms and in turn microorganisms can develop resistance systems to overcome the stress from toxic heavy metal ions. Additionally, some microorganisms can remediate heavy metal ions by transforming the active heavy metal

ions into inactive forms, which can be used in the bioremediation of contaminated areas. However, the inner interrelationship between microbial resistance to heavy metal ions and their remediation ability is still unclear. Therefore, we have summarized the heavy metal remediation and their detoxification pathways of microorganisms to uncover the interrelationship, which will contribute to finding more efficient bioremediation strategies and developing the next-generation bioremediation technology.

2. Heavy metal remediation strategies based on microorganisms

Anthropogenic activities and natural processes are the main sources of heavy metal pollution. With rapid development of industry and agriculture production, anthropogenic sources, such as fossil fuel combustion, mining, corrosion, smelting and waste disposal, greatly contribute to heavy metal pollution [11–14]. Active heavy metal ions including cadmium, chromium, lead, platinum can be generated from electrolysis depositions, anodizing-cleaning, milling and etching industries [15–17]. Printed circuit board (PCB) manufacturing will bring forth heavy metal wastes such as lead, nickel and tin [18]. Chromium and cadmium pollution can be induced by inorganic pigment manufacturing and petroleum refining [19,20]. All these anthropogenic activities will generate heavy metal-polluted wastewaters, sludge, and residues, which influence the health of human beings.

Nowadays, numerous bioremediation technologies have been developed to remove heavy metal ions from polluted water, which offer valuable strategies for on-site remediation. Choosing suitable biomaterial is a major challenge for heavy metal bioremediation. At present, living/dead microorganisms and surface modified biomass are the most widely utilized strategies.

2.1. Heavy metal remediation by living/dead microorganisms

Heavy metal removal by living/dead microorganisms own outstanding advantages including simple-to-use, low cost, high adsorption capacity and large availability. Among these microorganisms, bacteria, fungi, and algae are most widely used (Table 1).

Table 1
Heavy metal removal by living microorganisms.

Microorganism		Target metals	Optimum pH	Isotherm model	Capacity (mg/g)	Regeneration	Reference
Bacteria	<i>Pseudomonas aeruginosa</i>	Hg(II)	7.0	Langmuir	180	Y	[21]
	<i>Pseudomonas</i> sp.	Pb(II)	7.2	Langmuir	49.5	N	[22]
	<i>Bacillus</i> sp.	Pb(II)	5.0	Langmuir, Freundlich	15.4	N	[23]
	<i>Arthrobacter viscosus</i>	Cr(VI)	2.0	Langmuir	1161	N	[24]
	<i>Staphylococcus epidermidis</i>	Cr(VI)	5.0	Freundlich	56	N	[25]
	<i>Eichhornia</i> spp.	Cu(II)	5.0	Langmuir	28.5	N	[26]
	<i>Brevibacterium</i> sp.	Zn(II)	2.0	Langmuir	41.9	N	[27]
	<i>Rhodobacter capsulatus</i>	Zn(II)	7.0	Langmuir, Redlich-Peterson	164	N	[28]
	<i>Pseudomonaeruginosa</i>	Cd(II)	6.0	Langmuir, Freundlich	16.9	N	[29]
	<i>Bacillus cereus</i>	Cd(II)	5.0	Langmuir, Freundlich, Redlich-Peterson	31.9	Y	[30]
	<i>Ochrobactrum</i> sp.	Cd(II)	6.0	Langmuir	83.3	Y	[31]
Fungi	<i>Aspergillus niger</i>	Pb(II)	5.4	Langmuir	172	N	[32]
	<i>Penicillium simplicissimum</i>	Pb(II)	5.0	Langmuir	76.9	N	[33]
	<i>Aspergillus fumigatus</i>	Cr(VI)	5.5	Freundlich	48.2	N	[34]
	<i>Termitomyces clypeatus</i>	Cr(VI)	2.0	Langmuir, Freundlich	403	N	[35]
	<i>Penicillium brevicompactum</i>	Co(II)	5.0	Langmuir, Freundlich	54.6	N	[36]
	<i>Saccharomyces cerevisiae</i>	Cu(II)	5.5	Langmuir	16	Y	[37]
	<i>Trichoderma</i>	Cd(II)	6.0	Langmuir, Freundlich	21.7	N	[38]
	<i>Aspergillus niger</i>	Cd(II)	5.5	Langmuir	11	N	[39]
Algae	<i>Fucus vesiculosus</i>	Pb(II)	4.0	Langmuir, Freundlich	229	Y	[40]
	<i>Cladophora fascicularis</i>	Pb(II)	5.0	Langmuir, Freundlich	198.5	N	[41]
	<i>Sargassum</i>	Cu(II)	5.0	Langmuir	49	N	[42]
	<i>Cystoseira crinitophylla</i>	Cu(II)	4.5	Langmuir, Freundlich	160	Y	[43]
	<i>Spirogyra</i>	Cu(II)	5.0	Langmuir, Freundlich	87.2	N	[44]
	<i>Sargassum filipendula</i>	Cd(II)	6.0	Langmuir	7.8	Y	[45]
	<i>Ulva lactuca</i>	Cr(VI)	1.0	Langmuir, Freundlich, Redlich-Peterson, Koble-Corrigan	10.6	N	[46]

Y: yes; N: not mentioned.

2.1.1. Bacteria

Bacteria are the most abundant microorganisms in the earth, which can live in a wide range of environmental conditions. Because of their advantages such as small size, quick growth rate and easy to be cultivated, bacteria have been widely used to clean up heavy metal pollutants from the environment. As shown in Table 1, a series of heavy metal remediation methods based on bacteria including *Escherichia*, *Pseudomonas*, *Bacillus* and *Micrococcus* have been established. Generally, heavy metal ions can be adsorbed on the polysaccharide slime layers of bacteria through functional groups such as carboxyl, amino, phosphate and sulfate groups [21,47,48]. Heavy metal ions can bind on these groups and be accumulated with satisfactory adsorption capability. Generally, the uptake capacities of bacteria for heavy metal ions range from 1 mg/g to 500 mg/g. *Pseudomonas aeruginosa*, as a type of mercury-resistant strain, can selectively adsorb mercury ion with a maximum uptake capacity of nearly 180 mg/g [21]. These mercury ions are accumulated by cysteine-rich transport proteins which are abundant in sulfhydryl groups and have high affinity to mercury ions. *Pseudomonas* sp. I3 and *Bacillus* sp. PZ-1 can adsorb Pb(II) from wastewater [22,23]. The dead and living *Arthrobacter viscosus* biomass can adsorb Cr(VI) with high adsorption capacity, satisfactory recovery efficiency and regeneration ability. Both living and dead cells can reduce Cr(VI) to Cr(III) in aqueous solution. When the initial concentrations of Cr(VI) is lower than 100 mg/L, 100% Cr(VI) can be removed from aqueous solution under highly acidic pH (pH 1 and pH 2) [24]. The removal of Cr(VI) from aqueous solution by *Staphylococcus epidermidis* biofilms has been confirmed with high removal efficiency, which followed the Freundlich isotherm [25]. The *Eichhornia* spp. biomass collected from Chandola Lake can achieve 85.0% copper removal from 100 ppm Cu(II) containing solution [26]. The Zn(II) can be absorbed by bacterium *Rhodobacter capsulatus* with a maximal uptake capacity of 164 mg/g, which followed the Redlich-Peterson and Langmuir isotherms [28]. Both the living and dead cells of bacteria *Bacillus cereus* RC-1 have the biosorption capacity for Cd(II), with about 24.01 mg/g and 31.95 mg/g for living and dead cells, respectively [30].

Besides, extracellular polymeric substances (EPS) constituted by nucleic acids, proteins, lipids and complex carbohydrates also play an important role in the adsorption of heavy metal ions. The EPS on the microbial cell surface can protect the microbes against heavy metal toxicity by avoiding their entrance into the intracellular environment. The presence of cationic and anionic functional groups on EPS can efficiently accumulate heavy metal ions including mercury, cobalt, copper and cadmium ions [49–51].

The adsorbed heavy metal ions can be transported into the living bacterial cells metabolism-dependently and redox state of heavy metal ions can be changed to reduce their toxicity. In our research group, *Pseudomonas putida* SP1 isolated from the marine environment is resistant to high-level mercury and other heavy metal ions. The isolated *Pseudomonas putida* SP1 can absorb almost 100% of total mercury and reduce reactive Hg(II) to Hg⁰ vapor by reductase, which realize the bioremediation of mercury pollution in marine environments [52]. *Bacillus firmus* TE7 is capable of reducing Cr(VI) and oxidizing As(III) simultaneously after accumulating them from wastewater [53]. The alteration of physicochemical conditions of heavy metal ions by reductase from the living microbes after binding by functional groups can reduce the toxicity of heavy metal ions, which will further enhance their remediation ability towards heavy metal pollutions.

2.1.2. Fungi

Fungi can live under high heavy metal concentration and accumulate both micronutrients and heavy metals. Therefore, fungi have been widely used to adsorb heavy metal ions and exhibit high metal uptake ability. The chitin-chitosan complex, glucuronic acid, phosphate and polysaccharides in/on cells of fungi play an important role in heavy metal adsorption through ion exchange and coordination [54]. Different types of ionizable sites and various functional groups including

amine, carboxyl, hydroxyl, phosphate and sulfhydryl groups influence the adsorption capability and specificity of fungi strains to heavy metal ion. *Aspergillus niger* has been considered as suitable bio-sorbent to remove Pb(II) with high biosorption capacities [32]. The bio-removal of Cr(VI) by a native fungal isolate *Aspergillus fumigatus* from mine drainage has been studied. The maximum uptake of 48.2 mg/g Cr(VI) can be achieved under optimized conditions, which followed the Freundlich isotherm [34]. The acidic surface of *Termitomyces clypeatus* biomass can absorb Cr(VI) with help of carboxyl, imidazole, phosphate, sulfhydryl, and hydroxyl functional groups [35]. The unmodified yeast cell biomass of *Saccharomyces cerevisiae* has been investigated to remove Cu(II) from wastewater [37]. *Trichoderma* has been used for the removal of Cd (II), which well fits Langmuir and Freundlich isotherm model [38]. *Saccharomyces cerevisiae* can remediate copper, zinc and cadmium pollution under high salt environment and the adsorption ability can be enhanced with the help of sodium chloride [55].

2.1.3. Algae

Algae, as a type of photosynthetic organisms, can grow in both freshwater and seawater. Nowadays, algae have been reported to have good capability to absorb heavy metal ions. Heavy metal ions can be accumulated by different peptides generated by algae, which can also protect algae from the toxicity of heavy metal ions [56]. *Fucus vesiculosus* has been reported to adsorb Pb(II) with high efficiency, which can be described by Langmuir and Freundlich equation [40]. The adsorption features of *Cladophora fascicularis* have been investigated for Pb(II) removal from wastewater, which followed the Langmuir and Freundlich isotherm models. The maximum adsorption capacity of *Cladophora fascicularis* to Pb(II) is 198.5 mg/g at pH 5.0 and its biosorption kinetics followed the pseudo-second order model [41]. The free and immobilized marine algae *Sargassum* has been shown with good ability to clean up Cu (II) from aqueous solutions [42]. The copper biosorption by *Cystoseira crinitophylla* has been studied with very high adsorption capacity of 160 mg/g at pH 4.5. The sorption isotherms well fit the Langmuir and Freundlich model and the Thomas and Clark models can be used to describe the heterogenous ion exchange [43]. Macro-algae *Saccharina japonica* and *Sargassum fusiforme* have been investigated with good removal capacities for Cu(II), Cd(II), and Zn(II) in aqueous solution [57]. The green microalga *Desmodesmus* sp. has been employed for the bioremediation of Cu(II) and Ni(II) from wastewater with high capacity [58].

2.2. Heavy metal remediation by surface modified biomass

Microorganisms include bacteria, fungi, yeasts and algal grow quickly and can produce high yields of biomass. Therefore, microorganism-based biomass can be easily and cheaply obtained, which is suitable to adsorb active heavy metal ion from the polluted area [59]. To achieve effective remediation of heavy metal ions, biomass is required to own high metal adsorption capacity. The natural biomass without being pretreated because of its low/medium adsorption capacities cannot meet the requirement as satisfactory adsorbents for heavy metal remediation. Therefore, various techniques including acid/alkali-based treatment and thermal treatment methods have been established to increase the adsorption capacity of the biomass (Fig. 1).

2.2.1. Acid treatment

Biomass treated by acid can open additional adsorption sites for heavy metals. After acid treatment, biomass is protonated and positive charge density is improved, which provides a strong electrostatic attraction between biomass and negatively charged heavy metal ions. Additionally, biomass can be chemically coated by acid on its surface after treatment, which introduces plenty of binding sites for cationic metals. For example, after modification by polyacrylic-acid, the uptake capacity of Cd(II) by *Corynebacterium glutamicum* biomass increased by 3.2 times compared with untreated biomass [60]. The acid-treated biomass of *Trichoderma gamsii* showed maximum biosorption capacity

Fig. 1. Enhancing heavy metal removing efficiency of biomass through surface modification.

of 44.8 mg/g, which followed pseudo-second-order model. The sorption isotherms for Cr(VI) by acid-treated *Trichoderma gamsii* followed Freundlich and Langmuir isotherm [61].

2.2.2. Alkali treatment

Biomass after alkali treatment can increase negative charge on biomass surface, which will enhance the electrostatic attraction for positive charged heavy metal ions. After alkali treatment, the uranium biosorption capacity of fungal mycelia is much higher than untreated groups [62]. Generally, sodium hydroxide, calcium hydroxide, sodium bicarbonate, and ammonium hydroxide are mostly utilized for alkali treatment. Compared with nature *Mucor rouxii* biomass, pretreatment with alkali chemicals such as NaOH, NaHCO₃, and Na₂CO₃ can improve its adsorption capacity [63].

2.2.3. Thermal treatment

Thermal treatment can make additional metal binding groups exposed which increase the concentration of surface functional groups. After thermal treatment under an inert atmosphere, the carbon hydrophobicity in biomass can be increased by removing hydrophilic surface functionalities. Additionally, thermal treatment can also increase the porosity and surface area of biomass, which will enhance the adsorption capacity of biomass. The thermal treated *Saccharomyces cerevisiae* can be utilized to remove Cr(VI) ions from wastewaters [64]. Similarly, autoclaving of bacterial biomass can also enhance the adsorption ability of heavy metal ions [65].

Physical treatments of *Spirogyra* biomasses including heating, autoclaving and chemical treatments (acetic acid and sodium hydroxide) can increase biosorption of selenium in comparison with live biomass [66].

Table 2

Comparison of heavy metal remediation strategies.

Remediation strategies	Remediation mechanisms	Advantages	Disadvantages
Living/dead microorganisms	1, Binding by functional groups 2, Redox state change	1, Simple-to-use, 2, Low cost, 3, Environmental friendly 4, Can transform the valence of heavy metal ions into low toxic forms	Low/medium heavy metal adsorption capacity (1, Insufficient binding sites 2, Limited surface area 3, Weak electrostatic attraction between biomass and heavy metal ion)
Surface modified biomass	Binding by functional groups	High heavy metal adsorption capacity (1, Plenty of binding sites, 2, Enhanced electrostatic attraction between biomass and heavy metal ion 3, Bigger surface area)	1, Need modification 2, Limited ability to transform the heavy metal ions into low toxic forms

Physical pretreatments such as heating, freeze drying, autoclaving and chemical treatments using acids and alkali can increase the Cd(II) biosorption capacity of *Pleurotus florida* biomass. Among physical treatments, significant improvement of Cd(II) biosorption capacity of *Pleurotus florida* biomass can be achieved by freeze drying and NaOH-treated biomass show maximum cadmium biosorption among chemical treatments [67].

In conclusion, compared with surface modified biomass, active bioenzyme in living microorganisms contributes a lot to the detoxification of heavy metal ions through transforming them into low toxic forms but the binding sites and surface area are usually limited. Surface modified biomass can enhance the adsorption capacity of biomass through increasing binding sites, surface area and enhancing electrostatic attraction between biomass and heavy metal ions, but the bioenzyme is inactive after treatment which will inhibit the ability to transform high toxic heavy metal ions into low toxic forms. The comparison of heavy metal remediation strategies can be seen in Table 2.

2.3. Heavy metal remediation by microorganisms at pilot/full-scale

While many studies on the bioremediation of heavy metal are laboratory-based, there are some pilot/full-scale remediation technologies that have been established. The *Arthrobacter viscosus* biofilm has been verified that it can bind Cr(VI) in batch and column essays, which fits Freundlich model. A pilot bioreactor has been established after batch adsorption studies to clean up Cr(VI) from aqueous solutions with an average removal efficiency of 99.9% [68]. At 1995, Blowes and his coworkers first used sulfate-reducing bacteria to clean up heavy metal pollution in acid mine drainage at field scale [69]. Another full-scale sulfate-reducing bacteria (SRB) application on the remediation of heavy metal pollution has been achieved in Aznalcollar (Spain), where 30 mg/L Zn(II), 30 mg/L Cu(II) were contained in the wastewater [70]. A pilot-scale biological reactor system based on bacterium *Thauera selenatis* has been established to remove Se(II) and Ni(II) in drainage water at the Panoche Water District, San Joaquin Valley, California [71]. All above confirm the great potential of using microorganisms in heavy metal remediation and they can be applied at pilot/full-scale.

3. Resistance mechanisms of microorganisms to heavy metal ions

Metal ions such as cobalt and copper ions play important roles in microorganisms for their participation in diverse metabolic processes as components of various enzymes [72]. But excessive uptake of these metal ions will bring serious risks to microorganisms such as damaging cell membranes, inhibiting enzyme activity, damaging DNA and disrupting cellular functions. Most heavy metal ions such as lead, silver, and mercury ions are potentially toxic to microorganisms with no nutrient value. However, many microorganisms show specific resistance to some heavy metal ions. The microbial resistance is particularly relevant to microbial ecology. Sensitive microbial strains could be reduced or disappear under heavy metal stress and will be replaced by strains which can better adapt to and tolerate the toxicity of heavy

Fig. 2. Proposed detoxification pathways of microorganisms towards heavy metal ions [74–78].

Table 3

Resistance mechanisms of living microorganisms towards heavy metal ions.

Resistance mechanisms	Resistance molecular	Heavy metal ions	Microorganisms	Reference
Extracellular sequestration	Extracellular polymeric substances	Cu(II), Cd(II), and Zn(II)	<i>Desulfovibrio desulfuricans</i>	[47]
		Cd(II), Pd(II), and Zn(II)	<i>Alteromonas macleodii</i>	[82]
	Siderophores	Cu(II), Pd(II), and Zn(II)	<i>Pseudomonas aeruginosa</i>	[83]
		Pd(II)	<i>Ensifer adhaerens</i>	[87]
	Hydrogen sulfide	Cr(VI), Pd(II), and Zn(II)	<i>Pseudomonas aeruginosa</i>	[93]
		Cd(II), Ni(II), and Cr(VI)	<i>Desulfovibrio desulfuricans</i>	[90]
Intracellular sequestration	Polyphosphates	Cu(II)	<i>Sulfolobus solfataricus</i>	[94]
	Metallothionein	Cd(II)	<i>Anacystis nidulans</i>	[95]
		Cd(II), Zn(II)	<i>Synechococcus sp</i>	[75]
Active export	P-type efflux ATPase	Cu(II)	<i>Sulfolobus solfataricus</i>	[96]
		Zn(II)	<i>Sinorhizobium meliloti</i>	[97]
	ABC transporters	Hg(II), Cd(II), and Zn(II)	<i>Escherichia coli</i>	[98]
		Au(III)	<i>Cupriavidus metallidurans</i>	[99]
Enzymatic detoxification	Mercuric reductase	Hg(II)	<i>Pseudomonas sp.</i>	[100]
		Hg(II)	<i>Bacillus firmus</i>	[101]
	Catalase	As(III)	<i>Acinetobacter sp.</i>	[102]

metal ions. After many years of evolution, the microorganisms have physiological and chemical resistance mechanisms to overcome the toxicity of heavy metal ions [73]. Since microorganisms are the key factor in the bioremediation of heavy metals. The study of resistance mechanisms of microorganisms to heavy metal ions has a great contribution to the development of efficient bioremediation strategies. As shown in Fig. 2 and Table 3, the major detoxification pathways of heavy metal ions include extracellular sequestration, intracellular sequestration, active transport of the heavy metal and enzymatic detoxification, which can avoid heavy metal exposure or reduce their bioavailability.

3.1. Extracellular sequestration

Extracellular sequestration of active heavy metal ions can efficiently decrease their toxicity to microorganisms, which is the most widely used method for their removal. Heavy metal ions can be accumulated

by various biological structures including extracellular polymeric substances, siderophores, glutathione and bio-surfactants. EPS constituted by nucleic acids, lipids, proteins, and complex carbohydrates, have abundant metal-binding sites such as carboxylic, hydroxyl, amino, sulphhydryl and phosphate functional groups [74,79]. EPS are efficient bio-sorbents to various heavy metals including plumbum, copper, zinc, chromium and silver, which can influence the distribution of heavy metals in microorganisms [47,80–83]. Therefore, EPS can protect microorganisms against heavy metal toxicity and be utilized as an important bioremediation tool [50]. Siderophores like pyoverdine are organic ligands excreted by bacteria and fungi [76,84,85]. Siderophores have ability to accumulate ferric iron and form Fe-complexes, which help microorganisms survive under iron-deficient conditions. Beside ferric iron, siderophores can also bind other types of heavy metals including copper, zinc and nickel, which protect microorganisms from heavy metal toxicity [86–88]. Glutathione secreted by microorganisms

Fig. 3. Remediation mechanisms of microorganisms to heavy metal ions.

also has great ability to bind heavy metal ions. The heavy metal ions can be adsorbed with glutathione to form a complex and cannot enter living cells. The microbial production of hydrogen sulfide usually has significant effects on heavy metal detoxification. *Desulfovibrio desulfuricans* is unaffected by high concentrations of heavy metal ions with the help of hydrogen sulfide produced by itself. The secreted hydrogen sulfide in the extracellular environment will induce the precipitation of heavy metal ions and protect living cells from the toxicity of heavy metal ions [89–91]. Additionally, the cell wall of microorganisms is also a very important defense system against heavy metal toxicity. There are a great number of cationic and anionic functional groups on cell wall such as hydroxyl, amine, carboxyl and phosphate groups, which could avoid heavy metal ions entrancing into the intracellular environment by extracellular metal sequestration [92].

3.2. Intracellular sequestration

Once heavy metal ions cross cell wall and enter microorganisms, intracellular traps within the cytoplasm can sequester these heavy metal ions and prevent them from reaching toxic level. Therefore, sensitive cellular components can be protected from the exposure to heavy metal ions. Many microorganisms can transform heavy metal ions with the help of sulfides, cytosolic polyphosphates and cysteine-rich proteins [103,104]. On one hand, the active heavy metal ions can be transformed to form insoluble metal precipitates. Some bacteria and cyanobacteria can utilize cytosolic polyphosphates to deposit heavy metal ions [94]. On the other hand, heavy metal ions can be accumulated by cysteine-rich proteins like metallothioneins. When exposed to heavy metal ions, metallothionein can be overexpressed to overcome this stress. Cysteine residues in metallothionein may act as a sink for excess toxic heavy metal ions. For example, *Synechococcus* sp. can secrete metallothionein to bind Cd(II) and Zn(II) and reduce their toxicity to cells [105].

3.3. Active export of heavy metal ions

Transporting heavy metal ions away from the intracellular environment is another process to defend heavy metal stress, which can efficiently regulate intracellular concentrations of heavy metal ions with efflux systems [106]. These efflux systems have generally been found in different microorganisms, especially those isolated from metal-polluted environments. Generally, the expression of metal ion transporters in the efflux systems depends on bacterial species and heavy metal ions, which is regulated by special resistance genes on

chromosome or plasmid. These genes encoded membrane transporters which control the uptake and exclusion of heavy metal ions. There are numerous metal exporting proteins widespread in the cell membrane to achieve the efflux of heavy metal ions such as P-type efflux ATPase, proton-cation antiporters, ABC transporters and cation diffusion facilitator. The efflux of arsenite is regulated by an exporting protein on cell membrane with the help of ATPase [96,107]. Additionally, P-type efflux ATPase can help Gram-positive bacteria to export Cu(II), Cd(II), and Zn(II) [77]. ABC transporters (also called traffic ATPases) are able to mediate membrane translocation of heavy metal ions, which help microorganisms to overcome heavy metal stress [98,99,108].

3.4. Enzymatic detoxification

The biotransformation or chemical modification of heavy metal ions from a high toxic form to a less harmful form by enzyme contributes a lot to the resistance of microorganisms to heavy metal ions [78]. The redox state change of heavy metal ions through reduction or oxidation reactions can efficiently decrease their toxicity [100]. This defense pathway can be regulated by detoxification enzymes, which is also controlled by special resistance genes of microorganisms. Bacteria like *Bacillus* sp. show resistance to mercury ions through mercuric ion reductase [101]. Mercuric reductase reduces mercuric ion to metallic mercury, which further is released to the surrounding environment through the cell membrane [52]. Bacteria *Micrococcus* sp. and *Acinetobacter* sp. can oxidize the toxic As(III) into less soluble and harmless As(V) to decrease its toxicity [102].

4. Microorganism remediation mechanisms of heavy metal ions

Bioremediation of heavy metal ions is to minimize their toxicity. On one hand, heavy metal ions can be captured by functional groups in/on microorganisms. On the other hand, some heavy metal ions can be transformed from a toxic form to a less harmful form through redox state change by microorganisms. As a result, the toxicity of heavy metal ions can be efficiently decreased (Fig. 3).

4.1. Adsorption of heavy metal ions by functional groups

Heavy metal adsorption of microorganism is usually achieved by electrostatic interaction or binding with active components including polysaccharides, chitin, and cellulose derivatives. Some heterogeneous compounds located in or exterior to cell walls can accumulate heavy metal ions effectively, which further enhance the survival of microorganism under environmental stress. The adsorption of heavy metal ions by exopolysaccharide is energy independent and non-metabolic, which is caused by electrostatic interaction between heavy metal cations and the negative charged functional groups of exopolysaccharides [109]. Accumulation of heavy metal ions is mainly achieved by functional groups on active components including carboxyl, amine, hydroxyl, sulfhydryl and phosphonate. For example, copper(II), lead(II) and chromium(IV) can be accumulated by the amino and carboxyl groups through displacement of protons, which can be confirmed by the modification/blocking of these groups [110,111]. Carboxyl groups in EPS have been reported to bind heavy metals and the blocking of carboxyl groups lead to the decrease of metal binding [47]. Amine can be positively charged after protonation and form negatively charged metal complexes. Amine group in polysaccharides and chitin components contribute a lot to the binding of heavy metals [78]. The phosphoryl groups are also the main binding sites for heavy metal ions [112]. Cd(II) and Co(II) can be stored in polyphosphate in *C. humicola* cells, which play an important role in heavy metal remediation [104]. The heavy metal adsorption has been suggested to be an ion exchange process by functional groups. The ionic state of carboxyl, amino and phosphate groups will promote reactions with the positively charged metal ions, which may be the reason that pH values usually greatly influence the

adsorption capability of microorganisms towards heavy metal ions. Sulfhydryl compounds play an important role in heavy metal binding within cells. The K_{sp} of hydroxyl with Hg(II), Cu(II) and Cd(II) are 3.6×10^{-26} , 2.2×10^{-20} and 5.3×10^{-15} , respectively [113]. Compared with hydroxyl group, the K_{sp} of sulfhydryl group with Hg(II), Cu(II) and Cd(II) are 1.6×10^{-52} , 6.3×10^{-36} , 1.4×10^{-29} , respectively [114]. Therefore, the binding efficiency of sulfhydryl compounds to certain heavy metal ions are much higher than hydroxyl group. The metallothionein-like proteins, low molecular mass polypeptides with high cysteine content, show high binding ability to heavy metal ions, which protect microorganism from heavy metal toxicity. Significant correlation has been detected between mercury and sulfhydryl groups within the metallothioneins [115]. The binding ability of sulfhydryl compounds to heavy metal ions has also been investigated by atomic force microscope. All these indicate that the sulfhydryl content of microorganism plays important roles in the adsorption of heavy metal ions.

The biosorption of heavy metals by functional groups of microorganisms usually follows adsorption isotherm models. Generally, Langmuir and Freundlich models are the most widely used models to describe the heavy metal ions adsorption isotherm by microorganisms [51,116,117]. The classical Langmuir equation can be described as follow (1):

$$\frac{C_f}{q} = \frac{C_f}{q_{max}} + \frac{1}{bq_{max}} \quad (1)$$

q means the metal uptake and q_{max} means the maximum adsorption capacity. C_f means the final equilibrium solution concentration of mercury ion. b means the ratio of adsorption/desorption rates. When no migration of adsorbate molecules occurs on the surface of microorganisms, the biosorption of heavy metals will follow the Langmuir model. The Freundlich equation can be described as follow (2):

$$Q = KC_e^{1/n} \quad (2)$$

where Q means the adsorbed amount of heavy metal ion by microorganisms, K means adsorption equilibrium content indicative of adsorption capacity, C_e means the equilibrium concentration and n means the adsorption intensity. The Freundlich model is usually applied if the microorganisms own heterogeneous surfaces. Besides Langmuir and Freundlich models, Brunauer-Emmett-Teller model is utilized when the adsorption of heavy metal ions by microorganisms occurs in multi-layer [118]. Additionally, Scatchard plots have also been used to describe the adsorption of heavy metal ions [119]. Even though sometimes the adsorption behavior of heavy metals cannot be explained by above isotherm models under complicated conditions, the information about metal-uptake capability can still be provided.

4.2. Heavy metal remediation through redox state change

The detoxification of heavy metal ions by changing their redox state to less harmful form by microorganisms has played an important role in the remediation of heavy metal pollution from the environment. Many kinds of microorganisms can catalyze such reactions utilizing metals (Fe(III)) or metalloids (S^0) as terminal electron acceptors. The reduction of Cr(VI) to Cr(III) through enzymatic transformations has been widely studied in metal bioremediation by microorganisms. Insoluble hydroxides can be formed by reducing toxic Cr(VI) to Cr(III). SRB has been reported that its biofilms can reduce and precipitate Cr(VI) [120]. SRB based upflow anaerobic packed bed reactor has been developed to clean up Cu(II), Ni(II), Zn(II), Al(III), Fe(III), and Mg(II) from contaminated waters [121]. The heavy metal removal efficiencies of around 95% can be achieved by SRB for Ni(II), Zn(II), Cr(VI), and Cu(II) during the first 8 weeks with no inhibition of SRB growth [91]. The sulfide production, sulfate reduction and heavy metal precipitation with the help of SRB can efficiently remove heavy metals from polluted area. SRB can

increase sulfide concentration through sulfate reduction, which further generate insoluble metal sulfides to inactivate heavy metal ions in the wastewater. As described before, the K_{sp} of sulfhydryl group with Hg(II), Cu(II) and Cd(II) are very low so that the generation of stable insoluble metal sulfides will greatly reduce the risk of heavy metals ion. The SRB can also work with copper-iron bimetallic particles to enhance heavy metal removal efficiency and anti-toxicity ability [122]. *Bacillus amyloliquefaciens* can utilize glucose for Cr(VI) reduction under aerobic conditions [123]. Additionally, microbial consortium can couple the oxidation of phenol to Cr(VI) reduction [124]. The detoxification of mercury by enzymatic transformation has also been well studied. The Hg(II) can be reduced by mercuric reductase such as merA to the less toxic and volatile Hg^0 species [101,125]. For instance, *Pseudomonas putida* FB1 and *Pseudomonas* sp. B50A can reduce Hg(II) to Hg^0 with the help of merA reductase [126,127]. The engineered strains containing merA can increase mercury resistance and remediate mercury pollution to Hg^0 [128]. Microbial transformations of arsenic have been reported for the remediation of arsenic pollution. Unlike other metal ions, the inorganic form of arsenic is more toxic than its methylated derivatives. Some microorganisms can methylate arsenic compounds and decrease its toxicity. Additionally, As(III) can be oxidized to As(V) and attenuate its toxicity. Chemical oxidation of As(III) is very slow under most environmental conditions but microorganisms can accelerate this process. For instance, As(III) can be oxidized much faster than abiotic processes with help of *Thermus* sp. [129]. Additionally, As(V) forms insoluble sulfides more readily than As(III) when exposed to H_2S . Therefore, the oxidation of As(III) by microorganisms is a useful way of removing As from wastewater.

5. Bottlenecks and future application

Nowadays, heavy metal remediation by microorganisms has been utilized to remove heavy metal pollutions for its outstanding advantages of high-efficiency and low-cost. However, there are still many bottlenecks for its wide application. The molecular mechanism of heavy metal detoxification needs to be further elucidated to enhance the accumulation of heavy metal ions by microorganisms. The extracellular/intracellular sequestration, active export and enzymatic detoxification are the main resistance mechanisms of living microorganisms to heavy metal ions, which will decrease the toxicity of heavy metal ions and transform them into inactive forms. The precipitation of heavy metal ions by hydrogen sulfide and redox state change of heavy metal ions by reductase increase the resistance of microorganisms to heavy metal ions and meanwhile achieve the heavy metal remediation. There is a close inner interrelationship between microbial resistance system to heavy metal ions and their remediation ability. Most studies use the spiked metal matrix to investigate the adsorption capability of microorganisms. However, the survival of microorganisms in the natural environment is usually different with spiked specimens under different environmental conditions, which will limit the on-site application [130]. Meanwhile, the effectiveness of the bioremediation processes can also be influenced by environmental factors such as pH, temperature and ionic strength. For example, pH value influences the biosorption efficiency of heavy metal ions by changing the charge of functional groups on the cell surface and EPS [131]. Better remediation of heavy metal ions may be achieved by the combination of microorganisms with physical and chemical treatment, which can give microorganisms an optimized environment.

Considering the environmental conditions are quite complex, it is a big challenge to achieve the in-situ bioremediation of heavy metal ions. Generally, microorganisms can only resistant to special heavy metal ions. However, the microorganisms for the remediation of heavy metal ions in wastewater need to face the synergy toxicity of different heavy metal ions as well as cope with hydrological variations and complex contaminant mixtures. Additionally, some microorganisms which can remediate heavy metal pollution are conditional pathogenic and cannot

Fig. 4. Enhancing remediation efficiency of microorganisms to heavy metal ions through genetic engineering. A: phytochelatin surface display for enhanced metals bioremediation. Copyright 2018 American Chemical Society. B: expression of CadR on *Pseudomonas aeruginosa* for Cd(II) removal. Copyright 2018 Elsevier. C: heavy metals bioremediation by engineered lead-specific operon. Copyright 2014 American Chemical Society. D: bioremediation of mercury ion through surfacedisplay of carboxylesterase E2. Copyright 2016 Elsevier.

be widely used. To overcome these difficulties, genetic engineering is a good choice. Through overexpression of functional gene can increase the resistance of microorganisms to heavy metal ions. Multi-expression of different functional genes can help microorganisms overcome complex heavy metal toxicity. As shown in Fig. 4, the functional group can be located at more effective area through genetic engineering, which can also enhance the removal efficiency of heavy metal ions from the contaminated area [21,132–134]. The display of histidine oligopeptide on yeast can enhance their adsorption ability to heavy metal ions [135]. Through expressing *Pyrus calleryana* phytochelatin synthase, both the accumulation and resistance of heavy metal ions are enhanced for engineered *E. coli* bacteria [136].

Considering that genetic engineering can avoid the utilization of conditional pathogenic microorganisms as well as improve remediation efficiency by utilizing their functional gene, it has great potential in the future. Additionally, the combination of microorganisms with advanced material will also achieve high-efficient remediation of heavy metal ions, which need further investigation [137]. Due to the extremely low concentration of heavy metal ions in the environment, their quantification is also a major challenge. Therefore, the multifunctional microorganism system which can simultaneously realize remediation and detection of heavy metal pollution will also be the next consideration.

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