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REVIEW ARTICLE

Fungal-based remediation of carcinogenic heavy metals: A mini review

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ABSTRACT

Carcinogenic heavy metals are specific metals that significantly contribute to high prevalence of cancer and other cancer-related conditions in humans and other animals. These metals often enter the environment through mining, agriculture, disposal of waste and industrial processes posing significant threats to public health and environmental integrity. The removal of these metals by conventional remediation techniques are often expensive and may impose negative environmental impacts. This review explores the role of fungi (as individual colonies and in consortia) in the bioremediation of carcinogenic heavy metals, offering a sustainable and cost-effective alternative. Fungi possess unique physiological and morphological characteristics that enable them to withstand, accumulate, and convert various heavy metals through mechanisms like biosorption, bioaccumulation and enzymatic transformation. The paper discusses specific fungal species that effectively remediate carcinogenic metals such as arsenic, cadmium, chromium, lead, mercury and nickel. Despite recent advancements in fungal bioremediation over the past years, a comprehensive review detailing the fungal species utilized and the specific heavy metals targeted for remediation remains unavailable.

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INTRODUCTION

The rapid industrialization and urbanization especially during, the past century have resulted in a concerning rise in the contamination of soil and water sources with a wide variety of pollutants causing serious environmental pollution [1, 2]. Among these pollutants, carcinogenic heavy metals such as arsenic, cadmium, chromium, and nickel pose significant threats to human health and ecosystem stability [3-6].

Carcinogenic heavy metals are non-biodegradable elements with high atomic weights, and persistent nature that have been associated with the evolution of various cancers and other cancer-related diseases in humans and animals [3, 4]. They mostly leach and accumulate in the environment via untreated discharged wastes from anthropogenic activities (like mining, smelting, etc.), industrial processes (electroplating, paint, leather, metal and tanning), as well as chemicals discharged from farmland runoffs [7]. They get to human and animal tissues through various channels that include food chains, inhalation, direct intake or contact, and as well occupational exposure causing serious metabolic disorders [8]. The high rate of cancer occurrence in humans and animals is mostly attributed to the presence of these metals in their tissues triggering denaturing of DNA, imbalance of free radicals and antioxidants, subsequently leading to cell apoptosis [9, 10]. Arsenic, cadmium, chromium, lead, mercury and nickel are the notable carcinogens, however, they can be associated with other health ailments like neurological damage and respiratory problems [9, 11]. Prolonged contact with these metals results in the disruption of the body's tumor suppressor genes, deter repair processes and metabolic enzymatic due to oxidative stress [10]. Heavy metals are preserved in the environment for long periods due to their non-biodegradable nature, however, they can change into different oxidative forms or organic compounds, thus, reducing their toxicity and mobilizing or precipitating them [12, 13]. The remediation of heavy metals by physical and chemical techniques have often proven to be costly, energy-dependent and potentially harmful to the environment [13, 14]. In recent years, the use of living cells/tissues or their enzymes to mineralize or remove environmental

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contaminants have surfaced as a reliable, eco-friendly alternative for addressing heavy metal contamination [15-19]. Among the various organisms employed in bioremediation, fungi have attracted considerable interest due to their unique physiological and morphological characteristics that enable them to endure and accumulate lofty concentrations of heavy metals [20, 21-23].

Fungi are chemoheterotrophic eukaryotic organisms that exist as either microscopic unicellular molds or macroscopic multicellular mushrooms which are characterized with extracorporeal digestion and direct nutrient uptake [24]. Fungi possess several advantages over other microorganisms in the context of heavy metal bioremediation. Their extensive hyphal networks allow for efficient exploration of contaminated substrates, while their robust cell walls and diverse enzymatic systems contribute to their metal-tolerance and transformation capabilities [14, 25]. Furthermore, many fungal species can withstand and flourish in extreme conditions, thus, are suitable bioremediators for a wide variety of contaminated sites [26]. Fungal bioremediation (also referred to as mycoremediation) is usually achieved through enzymatic action in the presence of specific enzymes (like laccases, peroxidases, oxidoreductases and hydrolases), biosorption or bioaccumulation [27]. The elevated surface-to-volume ratio in fungi which facilitates efficient metal uptake and as well their ability to thrive in extreme environments make them an excellent choice for heavy metal bioremediation [14]. Dinakarkumar *et al.* [13] revealed fungi to have displayed great potentiality in the immobilization and transformation of heavy metals which was catalyzed by factors like pH, temperature, incubation period, ionic strength and metal concentration [27]. Several researches have proven that both the live or dead biomass of either microscopic or macroscopic fungi can be used in neutralizing heavy metals. However, the effectiveness of the remediation relies on the choice and application of suitable species for each specific metal [3, 28, 29]. Anjitha *et al.* [30] also reported that fungi have the capability to bear and neutralize heavy metals through various cellular processes that involve either binding the metal ions with specific functional groups on their cell wall, accumulating and forming ion complexes with their cell body, render the metals inert, convert, mobilize or immobilize them.

MECHANISMS OF FUNGAL BIOREMEDIATION OF HEAVY METALS

Fungi employ several mechanisms to immobilize or neutralize environmental heavy metals, these include:

Biosorption and Bioaccumulation

Biosorption is a passive, invertible and energy-independent process that focuses on the attachment of heavy metal ions to specific biochemical functional groups or extracellular polymeric substances (EPS) on fungal cellular surface [31]. It is the most prominent and effective remediation mechanism employed by fungi for the mineralization of heavy metals. It involves mechanisms such as ion exchange, complexation and physical adsorption and is specifically effective with the use of dead fungal biomass [13]. Several fungal species from a wide variety of genera which include *Aspergillus*, *Penicillium*, *Fusarium*, *Trichoderma* and others not mentioned exhibit high heavy metals biosorption capacity. For instance, *Aspergillus niger* and *Penicillium chrysogenum* have shown significant biosorption potential for metals like cadmium, mercury and lead which is due to their adsorption to functional groups (like carboxyl, amino, and phosphate) on the cell wall, which in turn reduce metals circulation and bioavailability [32]. Jamir *et al.* [33] also reported some yeast and filamentous fungal species to have high metal-sequestering capabilities. Bioaccumulation on the other hand, is an active energy-dependent process that is mostly irreversible which is associated with the entry and cellular buildup of heavy metals via specific channels and proteins into live fungal cells [31]. This mechanism often involves specific transport proteins that move metals to sites where they may be isolated, retained in vacuoles or attached to cellular proteins [13]. Smith *et al.* [34] revealed that *Trichoderma harzianum* displayed efficient bioaccumulation of significant concentrations of some specific heavy metals.

Biotransformation

This involves fungal transformation and conversion of heavy metals to less harmful or more volatile substances via various enzymatic processes associated with oxidation-reduction reactions [13]. The harmful effects of heavy metals is dependent upon their oxidation state which be altered through electron transfer between target metals and fungal cells, resulting in reduction or oxidation to less harmful forms [31]. A highly toxic hexavalent chromium (Cr(VI)) carcinogenic form, has been reported to be detoxified to a less harmful trivalent chromium (Cr(III)) by certain fungal species [13]. For instance, *Aspergillus niger* effectively converted hexavalent chromium to trivalent chromium when subjected to both aerobic and anaerobic conditions [32]. Sanyal *et al.* [35] also reported the transformation of metal ions Pb^{2+} and Cd^{2+} to carbonates crystals $PbCO_3$ and $CdCO_3$ respectively by *Fusarium oxysporum*, resulting from interaction of the ions with particular proteins released by the fungus.

Bioleaching

This is a technique that utilizes fungi to alter the solubility of metal ions by inducing precipitation reactions. This is achieved due to the ability of the fungi to produce organic acids that interact with metal ions to create metal oxalates or phosphates that eventually precipitate [36]. *Aspergillus niger* is a phosphate-solubilizing fungi that secrete citric acid and oxalic acid that are very vital in heavy metals precipitation. Metals like cadmium and lead form stable complexes with citric acid which in turn lower the toxicity [13]. It has been reported that *A. niger* can produce as much as 15 g/L of citric acid which is enough to immobilize and remove metals like cadmium [32]. In the case of oxalic acid secretion, fungi use this acid to precipitate insoluble metal oxalates that are easily eliminated from soils or aquatic ecosystems. The precipitation process occurs as a result of the transformation of soluble metal ions to solid metal oxalates that can be removed via sedimentation or filtration. The formation of lead oxalate from lead ion (Pb^{+}) was observed by Niehaus *et al.* [36] after inoculation of *A. niger* into a contaminated media which significantly decreased the lead concentration [37, 38].

Mycorrhizal Associations

Carris *et al.* [24] revealed that mycorrhizal fungi establish symbiotic associations with certain plants to improve the uptake and movement of heavy metals within the ecosystem. In this type of association, the fungi helps in expanding the root system of the plants to facilitate sufficient nutrient and pollutant absorption. The fungi may also assist in the uptake and stabilization of heavy metals in the plant tissues through release of organic acids and other chelating agents [13]. The presence of arbuscular mycorrhizal fungi in plant roots leads to the immobilization of heavy metals like arsenic and lead [36].

Co-metabolism and Synergistic Interactions

Ecosystems with complex combinations of contaminants may house fungal species that exhibit co-metabolism in which degradation of a certain pollutant catalyzes the neutralization of another [39]. Interestingly, fungi have been observed to simultaneously break down hydrocarbons and heavy metals under specific conditions in the soil [40]. Similarly, fungi improve heavy metal remediation by interacting with other microorganisms like bacteria, often leading to a sequential degradation pattern, where the metals are transform into simpler intermediate derivatives for the bacteria to further neutralize or vice versa [13].

FUNGAL SPECIES AND HEAVY METAL BIOREMEDIATION

Several fungal species from different genera have demonstrated great potential in the bioremediation of carcinogenic heavy metals. Some of these species include members from the genera *Aspergillus, Fusarium, Trichoderma, Penicillium, Phanerochaete, Trametes, Lentinus, Rhizopus*, among others [3,4,12,26,35,41-45].

Several studies have proven the potentiality of species from the genus *Aspergillus* in the effective mineralization of carcinogenic heavy metals. For instance, *Aspergillus niger, A. fumigatus, A. flavus, A. terreus, A. awamori, A. nidulans, A. candidus, A. sydowii* and *A. parasiticus* have exhibited significant effectiveness in immobilizing or neutralizing heavy metals like arsenic, cadmium, chromium, mercury, nickel and lead due to their robust growth and high metal tolerance [3, 4, 12, 13, 26, 32, 44, 46-53].

Penicillium species like *Penicillium chrysogenum, P. notatumi, P. piceum, P. restrictum, and P. expansum* have also shown significant potential in removal or stabilization of arsenic, cadmium, lead and mercury from contaminated soils and water [4, 12, 32, 44, 54, 55]. Their effectiveness is attributed to their high bioleaching and biosorption capacity as well as ability to produce metal-binding metabolites [13].

Furthermore, other fungal species have also been utilized in the successful remediation of carcinogenic heavy metals as presented in Table 1. Fungal species like *Phanerochaete chrysosporium, P. sordida, Rhizopus arrhizu, Trametes hirsuta, T. versicolor, Pleurotus ostreatus, Yarrowia lipolytica, Lentinus tigrinus* and *L. edodes* are as to be good mycoremediators of different carcinogenic heavy metals [42]. Joshi *et al*. [3] studied the effectiveness of heavy metals (lead, cadmium, chromium and nickel) removal using *Phanerochaete chrysosporium, Trichoderma viride* and *T. longibrachiatum* as biosorbents. Another study by Kumar *et al*. [4] also revealed an effective removal of cadmium, chromium and lead from sewage, sludge and industrial wastewater by *Rhizopus arrhizus* and *T. viride*. Species of *Chaetornium, Myrothecium, Stachybotrys, Rhizomucor, Rhizopus, Microdochium Fusarium, Alternaria* and *Geotrichum* have also been reported to thrive well in arsenic, lead and chromium contaminated environments [46, 56]. The fungal species degrade these metals by metabolizing and utilizing them as carbon and energy sources [57]. The employment of species like *Trichoderma harzianum*, *Fusarium solani*, *Culvularia* species and *Pleurotus* species through various bioremediation mechanisms have also been documented [26, 43, 44, 58]. Table 1 highlights the notable carcinogenic heavy metals remediated by some fungal species.

FUNGAL CONSORTIA FOR HEAVY METAL BIOREMEDIATION

A fungal consortium is a combination two or more fungal species or a mixture of fungal species with other microorganisms like bacteria that is commonly used in the break down of environmental contaminants like heavy metals. The use of fungal consortia in the removal of heavy metals by cellular adsorption and accumulation is more efficient than using individual fungal strains [68,69]. Recent researches have outline the efficiency of integrating varieties of fungal species with complementary degradation abilities for effective heavy metals removal from the ecosystem [70]. Efremenko *et al*. [69] developed four fungal consortia to be used in the removal of heavy metals (cadmium, chromium, lead, nickel and zinc), which were detoxified at varied concentrations and levels. The first consortium (*Aspergillus niveus* and *A. flavus*) almost completely neutralized chromium, the second (*A. flavus* and *A. niger*) and third (*A. niveus* and *A. niger*) consortia showed a slight variation in the neutralization of the metals, and finally, the fourth consortium (two strains of *A. fumigatus* and *A. flavus*) effectively detoxified hexavalent chromium (Cr(VI)) and divalent cadmium (Cd(II)) [71,72]. Hassan *et al*. [73] established a consortium of 13 strains various species of fungi (*Perenniporia subtephropora, A. fumigatus, A. niger, Phanerochaete concrescens, Cerrena aurantiopora, Fusarium equiseti, F. chlamydosporium, Paecilomyces lilacinus, Trametes versicolor, Antrodia serialis, Daldinia starbaeckii, Penicillium cataractum* and *Polyporales* species) to remediate arsenic, chromium and three other non-carcinogenic heavy metals from contaminated soil as shown in Table 2. The same consortium was subsequently used in the partial removal of nickel, lead and zinc in another study [74]. A mixed culture of *A. flavus, A. terreus, Talaromyces islandicus* and *Neurospora crassa* almost completely degraded lead and nickel from wastewater [75]. In a different research carried out by Hassan *et al*. [76] two consortia one made up of highly tolerant fungi (*Perenniporia subtephropora, Daldinia starbaeckii, A. fumigatus, A. niger, Phanerochaete concrescens, Cerrena aurantiopora, Fusarium equiseti, Trametes versicolor* and *Polyporales* species) and the other of moderately tolerant fungi (*Paecilomyces lilacinus, Antrodia serialis* and *Penicillium cataractum*) were developed for the bioleaching of arsenic, chromium and two other metals. Dell'Anno *et al*. [53] in their study used both individual and mixed cultures of *A. niger* and *Trichoderma* species with bacterial strains to detoxify arsenic, zinc and cadmium contained in bay sediments. Fungi may display high effectiveness in heavy metal removal while in association with bacteria [67]. Current studies have shown great achievement in the use of fungal-bacterial based consortia for the neutralization of heavy metals. In this type of association, the fungi having extensive enzymatic capabilities initiate the dissociation of the heavy metals which are subsequently metabolized by the bacteria. The overall effectiveness of bioremediation efforts can greatly be improved by following the aforementioned stepwise degradation technique during treatment of mixed contaminant waste streams [70]. For example, a study observed the capability of a consortium of *A. fumigatus, A. terreus* and a bacterium *Paenibacillus dendritiformis* to have efficiently mineralized cadmium [77]. Table 2 presents some of the consortia employed in the mycoremediation of carcinogenic heavy metals.

Table 1. Fungal species with heavy metal-remediation potential

Fungal Species	Carcinogemic Heavy Metals	Reference
Absidia cylindrospora	As, Cd, Pb	
Agaricus bisporus	Cd, Hg, Ni, Pb	
A. bitorquis	Cd, Ni, Pb	
A. macrosporus	Cd, Hg	
Alternaria alternata	Cd, Cr, Ni	
Amanita rubescens	Cd, Pb	
Atmillaria mellea	Cd, Ni, Pb	
Ascochyta betae	Cr	
Aspergillus awamori	Cd, Cr, Ni, Pb	
A. candidus	As	
A. flavus	Cd, Cr, Ni, Pb	
A. fumigatus	Cd, Cr, Ni, Pb	
A. foetidus	Cr	
A. gracilis	Cd, Pb	
A. nidulans	Cd, Cr, Pb	[59-61]
A. niger	As, Cd, Cr, Hg, Ni, Pb	
A. ochraceus	Cr	
A. oryzae	Cr	
A. penicillioides	Cd, Pb	
A. restrictus	Cd, Pb	
A. sydowii	Cr	
A. terreus	Cd, Cr, Ni, Pb	
A. versicolor	Cr, Ni, Pb	
Beauveria bassiana	Pb	
Bjerkandera adusta	As, Pb	
Candida utilis	Cr	
Circinella species	Ni	
Cladonia rangiformis	Pb	
Corollospora lacera	Cd, Pb	
Cunningghamella echinulata	Ni, Pb	
Curvularia lunata	Cd, Cr	
Drechslera rostrata	Cr	
Emericella species	As	
Fomitopsis meliae	As, Pb, Cd	
Funalia trogii	Cd, Hg	
Fusarium oxysporum	As	
F. solani	Cr, Ni	
Ganoderma multipileum	Cr	
Gllocladium roseum	Cd	
Gloeophyllum sepiarium	Cr	
Glomus intraradices	As, Cd, Cr, Pb	
Hirsutella species	Cr	[62,63]
Inonotus hispidus	As	
Kalmusia italica	Cr, Ni, Pb	
Laccaria bicolor	As, Cd, Pb	
Lactarius piperatus	Cd	
Lentinula edodes	Cd, Pb	
Lentinus crinitus	Cr, Pb	
Lentinus edodes	Cd, Cr, Pb	
Metarhizium anisopliae	Pb	
Monodictys pelegica	Cd, Pb	
Mucor hiemalis	Cd	
Mucor rouxii	Cd, Ni, Pb	
Neocosmospora species	As	
Neuropora crassa	Pb	

Table 1. Fungal species with heavy metal-remediation potential (Cont.)

Fungal Species	Carcinogemic Heavy Metals	Reference
Paxillus involutus	As, Cd, Pb	[7,12,64,65]
Penicillium chrysogenum	Cd, Cr, Ni, Pb	
P. rubens	Cd, Cr	
P. janthinellum	As	
P. canescens	As, Cd, Hg, Pb	
P. purpunogenum	Cr	
P. simplicissimum	Cd, Pb	
P. notatum	Cr	
P. decumbens	Cd, Cr, Ni	
P. digitatum	Cd, Pb	
P. verrucosum	Pb	
Phanerochaete chrysosporium	As, Cd, Hg, Ni, Pb	
Phelliinus weirii	Ni, Pb	
Phlebia brevispora	Cd, Ni, Pb	
Phlebia floridensis	Cd, Hg, Ni, Pb	
Pisolithus tinctorius	As, Cd, Pb	
Pleurotus florida	Ni, Pb	
P. floridianus	Cd, Ni, Pb	
P. ostreatus	As, Cd, Cr, Hg, Ni, Pb	
P. sajor-caju	Cd, Hg, Pb	
P. sapidus	Cd, Ni, Pb	
Polyporus frondosus	Cd, Ni, Pb	
P. sulphureus	Cd, Ni, Pb	
Pycynoporus sanguineus	Cd, Pb	
Pyrenochaeta cajani	Cr	
Rhizoctonia solani	Cr	[66.,67]
Rhizophagus irregularis	As, Cd, Pb	
Rhizomucor species	As	
Rhizopus arrhizus	Cd, Cr, Ni, Pb	
R. cohnii	Cd	
R. microsporus	As, Cd, Pb	
R. nigricans	Cr, Pb	
R. oligosporus	Cd	
Rhodotorula mucilaginosa	Pb	
Saccharomyces cerevisiae	Cd, Cr, Ni, Pb	
Saprolegnia delica	Cd, Pb	
Serpula himantioides	As, Cd	
Sterigmatomyces hetophilus	Cd, Pb	
Talaromyces helices	Cd	
Trametes pubescens	Ni Pb	
T. hirsuta	Cr	
T. versicolor	As, Cd, Hg, Pb	
Trichoderma asperellum	As	
T. ghanense	As, Cd, Pb	
T. longibrachiatum	Cd, Cr, Ni, Pb	
T. viride	Cd, Cr, Ni, Pb	
Trichosporon cataneum	Cr	
Volvariella diplasia	Cd, Ni, Pb	
Volvariella volvacea	Cd, Ni, Pb	
Yarrowia species	Hg	

As=arsenic, Cd=cadmium, Cr=chromium, Ni=nickel, Hg=mercury, Pb=lead

Table 2. Fungal consortia with heavy metal-remediation potential

Fungal Consortia	Carcinogenic Heavy Metal	Reference
Aspergillus niveus, A. flavus, A. niger	Cd, Cr, Ni, Pb,	[61,68,69,71-77]
A. flavus, two strains of *A. fumigatus*	Cd, Cr	
Ascomycota, Basidiomucota fungi	As, Cr	
A. flavus, A. terreus, Talaromyces islandicus, Neurospora crassa	Ni, Pb	
Mucor hiemalis, T. viride	Cd, Pb	
Perenniporia subtephropora, A. fumigatus, A. niger, Phanerochaete concrescens, Cerrena aurantiopora, Fusarium equiseti, F. chlamydosporium, Paecilomyces lilacinus, Trametes versicolor, Antrodia serialis, Daldinia starbaeckii, Penicillium cataractum, Polyporales species	As, Cr, Ni, Pb	
Perenniporia subtephropora, Daldinia starbaeckii, Phanerochaete concrescens, Cerrena aurantiopora, Fusarium equiseti, A, niger, A. fumigatus, Trametes versicolor, Polyporales species	As, Cr	
Antrodia serialis, Paecilomyces lilacinus, Penicillium cataractum	As, Cr	
A. fumigatus, A. terreus, Paenibacillus dendritiformis (a bacterium)	Cd	

As=arsenic, Cd=cadmium, Cr=chromium, Ni=nickel, Hg=mercury, Pb=lead

CONCLUSIONS

In conclusion, a diverse range of fungal species have been identified as highly effective in immobilization and detoxification of carcinogenic heavy metals either as individual pure or mixed cultures or in collaboration with other microorganisms through mechanisms like biosorption and bioaccumulation. This has greatly contributed to the mitigation of the environmental impacts these metals cause. The notable fungal species employed in carcinogenic heavy metal remediation are native to the following genera *Aspergillus, Penicillium, Rhizopus, Trichoderma, Phanerochaete, Trametes, Fusarium* and *Pleurotus*. However, more species can be uncovered via interdisciplinary collaboration between mycologists, environmental scientists, geneticists, and engineers which will aid in the advancement of fungal bioremediation technologies leading to innovative approaches that combine the natural capabilities of fungi with cutting-edge technologies to potentially improve clean up of contaminated environments.

DATA AVAILABILITY STATEMENT

No data was used for the research described in the article.

CONFLICT OF INTEREST

The author declares that there is no conflict of interest with any individual, institution, or organization in the preparation, evaluation, or publication of this study.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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