



Recent Advances of Fungal Sorbents in Environmental Sustainability and Ecotoxicological Monitoring

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ABSTRACT

The aquatic systems are significantly introduced with toxic pollutants due to various industrial performances. The removal of heavy metals using several conventional methods is replaced with modern tools employing biological material such as bacteria, fungi as potential biosorbent. This comprehensive review was attempted to compile the scattered information on the ability of fungus in the selective sequestration of metal toxicants. Cellular properties and mode of action displayed by the active functional groups of fungal sorbents and the factors that contribute for bio sorption by dead and live fungal biomasses are elaborately discussed. The concerns correlated to fungal bio sorption are examined and a possible solution required to achieve a sustainable environment are evaluated. Though, few literatures on the metal removal efficiency of fungal biosorbents are reported, very little attention has been revealed regarding their industrial utilization and the mechanism of metal sequestration. This review creates an overall insight regarding the present state of fungal applications as a biosorbent and the challenges and solution they offer in treating polluted environment.

Key Words: Fungal biomass, Heavy metals, Biosorption mechanism, Adsorptive properties, Ecotoxicological sustainability.

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INTRODUCTION

Rapid rise in industrialization and urbanization had egressed as a significant threat to aquatic environment due to the direct discharge of massive pollutants as waste into the ecosystem [1, 2]. The most diverse pollutants in industrial effluents include inorganic heavy metals and organic dyes, which are extremely tenacious and can have a prolonged negative impact on aquatic organisms. Industrial effluents often contain several potential hazards that could not be refined through current purification methods [3]. The primary pollutants emitted by industrial sites contains toxic metals such as Cu, Cr, Cd, Hg, Ni, Pb, Zn, etc. [4]. Exhausted metals accumulate in living tissues via the food chain and induce toxicity to all the life forms causing adverse impact on public health [5, 6, 7 and 8]. Heavy metal recovery using conventional methods is neither cheap nor ecologically sound, as incidence of toxicological consequences were recorded due to excessive chemical utilization [9]. Therefore, government regulatory laws are heavily relying on industrial sectors to implement novel and advanced water treatment techniques [3, 10]. Current quest for a novel, innovative, adaptable and renewable technique for metal remediation has attracted focus on effluent purification [11, 12]. The level of concentration of toxic metals in the effluent must be scaled down to the permissible limits before it causes irreplaceable collapse to the ecosystem [13, 14].

In this endeavor, biosorption has emerged as an attractive technology and a prominent substitute to current wastewater treatment methods due to its low capital investment, effectiveness in treatment, minimal generation of secondary waste, slow processing period, and minor toxicity concerns [15, 16]. Biosorption is a metabolism-independent process in the type of mechanism involving a physiochemical interaction that mainly occur in the cell wall [17]. The biosorption process consists of a liquid phase (usually water) containing dissolved compounds or sorbate (metal ions) and a solid phase (bio-sorbent) with active sites on its surface. Due to the strong affinity of sorbent for sorbate species, the latter is drawn and bonded onto its surface through a distinct process. The method is continued until the amount of solid-bound sorbate and sorbate left in the solution achieve equilibrium.

Microorganisms such as bacteria, fungi, algae, and some plant and animal waste biomasses have the ability to remove heavy metal ions and promote their transformation to lesser toxic forms [18]. Microorganisms are recognized as a large spectrum of species that possess desirable characteristics to act as an ideal

sorbent for most metal pollutants. Physiochemical reaction between active sites of the microorganism and metal ions distributed in polluted water occurs through complexation, chelation, ion exchange, [19]. Several Bacterial species, such as *Chryseobacterium sp.*, *Comamonas sp.*, *Delftia sp.*, *Enterobacter sp.*, *Ochrobactrum sp.*, *Providencia sp.*, and *Stenotrophomonas sp.*, have showed remarkable ability to adsorb heavy metals from the culture medium [20, 21, 22]. *Enterobacter cloacae* KJ-46, *E. cloacae* KJ-47, *Viridibacillus arenosus* B-21, and *Sporosarcina soli* B-22 have been reported to be effective for Cu, Cd, and Pb degradation [23]. *Aspergillus sp.* are capable of removing Cr and Ni from effluent discharge through biosorption [24]. A yeast strain ES10.4 isolated from activated sludge was employed for reduction of metals such as Cu, Hg, Cd, and Pb [25]. However, compared to fungus, application of bacteria in biosorption is reported to be limited due to their poor resistance to metal [26]. The use of fungal biomass in wastewater treatment to remove organic and inorganic pollutants has shown to be an excellent alternative due to the higher secretion of intracellular and extracellular metal chelators and anti-oxidative defense system [27, 28]. Based on this foundation, the purpose of this review is to document the metal chelating properties of fungi from toxicologically polluted aqueous environments. Review also discusses the potential advantages, limitations, scope, and scientific value of fungal biosorption.

FUNGI AS A BIO-SORBENT

Fungi are the most diverse kingdom, containing species that comprise both unicellular and multicellular beings of ecological significance [29]. Multicellular fungi possess growth forms that are distinct from those of plants and animals [17, 30]. Fungal cell walls are rich in functional groups and bioactive compounds that contribute in biosorption [31, 32]. Metal-binding capabilities, and intracellular accumulation are reported to be higher in fungus due to the involvement of metal transport proteins in the metal tolerance either by extruding toxic metal ions from the cytosol out of the cell or by allowing metal sequestration into vacuolar compartment [33, 34, 35]. *Candida palmiophila* KB-6 isolated from tea soil was shown to be less tolerant to Cd, Hg, Ag, Ni and many other metals (excluding Pb) compared to *Cryptococcus sp.* AH-13 [36]. The resistance profile of *Candida parapsilosis* to heavy metals such as Cr, Cu, Hg, Ni, Pb and Zn has been documented [26]. Furthermore, few *Saccharomyces sp.* isolated from three different fruits were found to exhibit resistance to metals such as Cd, Cu, Mn, Zn, and Ag [37]. Both heavy metal susceptibility and removal by *Rhodotorula mucilaginosa* was exhibited for Hg, Cu, Pb [38]. The potentiality of fungi to synthesize exoenzymes for complex carbohydrate assimilation without prior hydrolysis makes them capable of removing contaminants like heavy metals from aqueous solutions in significant amounts [39, 40].

Table 1: Biosorption capacities and removal efficiency of various fungal species in waste water treatment

Sl. No.	Fungal species	Metal pollutants	Pretreatments	Biosorption capacity (mg/g)	Removal efficiency (%)	References
1.	<i>Aspergillus fumigatus</i>	Th	Biomass	370	-	[200]
2.	<i>Aspergillus fumigatus</i> RH05	Zn	Non-growing live biomass Oven dried biomass	-	59.72 59.81	[123]
3.	<i>Aspergillus flavus</i> NA9	Zn	-	287.8	-	[201]
4.	<i>Aspergillus flavus</i> RH07	Zn	Non-growing live biomass Oven dried biomass	-	40.89 82.38	[123]
5.	<i>Aspergillus flavus</i> strain KRP1	Hg	-	-	97-98.5	[202]
6.	<i>Aspergillus japonicus</i>	Fe Cr Ni Hg	Biomass	1.34 1.18 1.89 1.23	-	[203]
7.	<i>Aspergillus lentulus</i>	Cr Cu Pb Ni	Live	-	79 78 100 42	[204]
8.	<i>Aspergillus niger</i>	Cu	Mycelium pellets Aerial mycelia Spores	8.1 20.02 27.3	-	[205]
9.	<i>Aspergillus niger</i> 405	Cu Ni	-	4.4 2	-	[206]
10.	<i>Botrytis cinerea</i>	Cu Cd	-	9.23 17.03	-	[207]

11.	<i>Funalia trogii</i>	Hg Cd Zn	Heat inactivated immobilized	402.2 191.6 54.0	-	[208]
		Hg Cd Zn	Immobilized live	333.0 164.8 42.1		
12.	<i>Klebsiella sp.</i> 3S1	Pb	Biomass	140.19	-	[209]
13.	<i>Lentinus edodes</i>	Hg Cd Zn	Live	336.3 78.6 33.7	-	[210]
		Hg Cd Zn	Inactive pellets	403.0 274.3 57.7		
14.	<i>Lentinus sajor-caju</i>	U	Alkali treated Untreated Heat treated	378 268 342	-	[211]
15.	<i>Mucor hiemalis</i>	Hg	-	-	99	[212]
16.	<i>Mucoromycote sp</i>	Cd	-	79.67	-	[213]
17.	<i>Paecilomyces lilacinus XLA</i>	Cd	-	77.61	-	[213]
18.	<i>Paecilomyces variotii</i>	Hg	-	26.0	86	[214]
19.	<i>Penicillium canescens</i>	Cd Pb Hg As	-	102.7 213.2 54.8 26.4	-	[107]
20.	<i>Penicillium chrysogenum</i>	Cd Zn Cu Pb	Biomass	21.5 13 11.7 96	-	[215]
21.	<i>Pencillium chrysogenum</i>	U Sr Cs	Mycelial pellets	-	62 39 50	[216]
22.	<i>Penicillium sp.</i>	Sr U Th	Bio-nanocomposites of fungus-Fe ₃ O ₄	100.9 223.9 280.8	-	[217]
23.	<i>Phanerochaete chrysosporium</i>	Cd Pb	-	15.2 12.34	-	[218]
24.	<i>Phanerochaete chrysosporium</i>	Cu	Live and dead biomass	-	40-60	[219]
25.	<i>Phanerochaete chrysosporium</i>	Pb	Resting cells	80	-	[220]
26.	<i>Phanerochaete chrysosporium</i>	Zn	Treated with elemental selenium particles	-	88.1	[221]
27.	<i>Phanerochaete chrysosporium</i>	As	Pellets	-	100	[222]
28.	<i>Phanerochaete chrysosporium</i>	Zn Se	Immobilized pellets	-	88.1 56.2	[221]
29.	<i>Pleurotus sapidus</i>	Cd Hg	Immobilized live	96.57 207.89	-	[205]
		Cd Hg	Heat inactivated	127.12 287.43		
30.	<i>Rhizopus arrhizus</i>	Cu	Freeze dried Live Oven dried	191 165 190	-	[223]
		Cd	Freeze dried Live Oven dried	262 243 220		

		Sr	Freeze dried Live Oven dried	424 342 271		
31.	<i>Rhizopus arrhizus</i>	Ni	Living biomass	618.5	-	[224]
32.	<i>Rhizopus arrhizus</i>	U Sr Cs	Mycelial pellets	-	90 44 41	[216]
33.	<i>Rhizopus arrhizus</i> <i>Env 3</i>	Ni	Living biomass	618.5	-	[224]
34.	<i>Rhizopus oryzae</i>	Cu	Viable Pretreated	19.4 43.7	-	[225]
35.	<i>Rhizopus oryzae</i>	Cu	Biomass	34.84	-	[226]
36.	<i>Rhizopus nigricans</i>	Pb	Self-immobilized fungus	83.5	-	[227]
37.	<i>Rhizopus oligosporus</i>	Cu	Biomass	79.37	-	[228]
38.	<i>Rhodotorula mucilaginosa</i>	Hg	-	-	69.9	[38]
39.	<i>Trametes trogii</i>	U	Modified pellets Native pellets	447.4 238.2	-	[229]

CELL WALL STRUCTURES AND ITS ADSORPTION PROPERTIES

The frontiers of fungal cell wall research are transitioning from a descriptive phase that outlines the main components of fungal walls to a more dynamic assessment of how the various cellular components assemble and modify in response to an external stimulus [41]. The molecular composition of the cell wall is a crucial factor that determines the ability of fungal bio sorption. The fungal cell wall is organized into various layers, whereas all the layers are deposited on the most conserved innermost layer. The fungal cell wall is a highly malleable skeleton that is essential for the cell's integrity, permeability, and survival [42]. The cell wall contributes up to 30% of the fungus's dry mass, with polysaccharides making up the majority of it, to which different proteins are glycosylated. Composition of cell wall includes glucans (50-60%), chitin (2-20%), chitosan and glycosylated proteins (30-50% in yeast and 20-30% in filamentous fungi) [43], with considerably lesser quantities of lipids, pigments, and inorganic salts [44].

Fungal cell structures are composed of matrix components that are connected to form scaffolds of fibrous polysaccharides [45, 46]. Fungi can accumulate metals into their spores and filaments through the cell wall, which is essential for the survival and functioning of fungi [47]. Factors such as capability of the fungus to survive on extremely polluted environment; ability to exhibit metabolic reduction of heavy metal contamination; easy culturable methods are the additional advantages for employing fungal adsorbents in waste water treatment [48]. Potential of the bio-sorbent is determined by the ionic state of the biomass while the effectiveness depends on its porous structure and polarity. Fungal biomass has drawn tremendous attention as a metal chelating agent because of the increased presence of cell-wall material and also due to the diversity of active sites available for metal sequestration [17]. Active uptake of metal ions through the cell wall of fungi undergoes the process of cellular precipitation and valence conversion. The cell surface is negatively charged due to the presence of numerous anionic structures, such as glucan and chitin, which facilitates the binding of metal cations [33,47]. The presence of chitin-chitosan, glucuronic acid, phosphate, and polysaccharides on fungus cells contributes for heavy metal adsorption via ion exchange and coordination. Functional groups, including amine, carboxyl, hydroxyl, phosphate, and sulfhydryl, play a vital role in the adsorption of heavy metals and dyes [46, 49]. The surface of the fungal cell wall is rigid and composed of various components like lipids, polysaccharides and peptidoglycans which are rich in metal-binding ligands (e.g., -OH, -COOH, -HPO₄²⁻, SO₄²⁻, -RCOO⁻, -NH₂, and -SH) for the removal of inorganic metals. Among these functional groups, amines are active in metal uptake as it binds to anionic and cationic metal species through electrostatic interaction and surface complexation respectively [50]. The study by Joo et al. on lyophilized cells of *P. eryngii* have revealed the presence of carboxylic, amino, hydroxyl and methyl groups which have shown biosorption for the metals Cd(II) and Pb(II) [51]. Heavy metal remediation is mediated by a complex combination of natural polymers mainly composed of polysaccharides, nucleic acids, lipids and proteins [52]. Few researches on fungus have reported the presence of amino, thiol, hydroxide, phosphate and carboxylic groups on the cell wall of *P. ostreatus* which helps in the biosorption of heavy metals [53, 54, 55] Metal binding proteins and peptides mediate the biosorption of metals which was demonstrated by the utilization of *Candida lipolytica* derived lipoprotein in the remediation of cadmium, lead and zinc [56].

VIRTUE OF FUNGAL BIOSORBENTS

A majority of fungal bio-sorbents are safe due to their non-pathogenic properties and are readily accepted by the public for their practical applications [48, 57]. Since fungal biomass is considered as a low-value by-product, and have good potential in various applications with promising growth attributes in diverse environments, it can act as an excellent source for the supply of non-living material for metal bio-sorbents [48, 58, 59]. The study by Park *et al.* reported the practical application of dead biomass of *Aspergillus niger* showing complete removal of Cr (VI) when placed in contact with synthetic wastewater containing Cr(VI) [60]. Because of its filamentous structure, the separation of biomass from liquid media through filtration is relatively an easy process [40]. Many filamentous fungi are insensitive to low nutrition and can grow under diverse conditions such as temperature, aeration, pH [39, 61]. In contrast, yeast is widely accepted as a popular system for studying biosorption because of their a) desired actions during the molecular interaction between metal and microbe, b) ease of gene transformation, and c) due to the availability of a whole genomic sequence [62,63].

MECHANISM OF FUNGAL BIOSORPTION

Fungal cell surfaces can be considered as a mosaic of several active sites where metal coordination complexes can occur. Because of the chemical properties and structural arrangement of the fungal cell wall, metals can be deposited on its surface or within its structure before entering the cellular core or might be bound together by other cytoplasmic substances and organelles [19, 64]. Metal absorption onto fungal cell surfaces is a two-step process, one is the stoichiometric interaction between the active sites and metal ions, and the other is progressive deposition of metals on cell surface [17].

Biosorption mechanisms can be classified into two categories based on the cell's metabolism- Metabolism dependent and metabolism independent mechanism. Metabolism dependent is an active metal uptake or bioaccumulation process that happens in living cells and are driven by the energy. Whereas metabolism independent is a passive metal uptake process which occurs both in live and dead cells [65]. The production of metal-binding proteins is facilitated by living cells, where the cells first bind randomly to the metal ions using the extracellular polymers followed by an active transport of metals inside by specific transmembrane transporter proteins. Once transported inside the cells, these metals are detoxified by binding to specific metal-binding proteins and later transports these metal protein complexes into the vacuoles for sequestration. Whereas dead cells absorb metals through functional groups on the surface [66, 67, 68]. Dead cells are widely accepted over live due to their high environmental resistance, greater toxicity tolerance, less demand for nutrient supply to obtain their active state, and easy recovery of loaded metal ions and simpler reprocessing steps for the obtained biomaterial [69, 70]. The passive intake of metals is relatively quick and reversible [65, 68]

Intracellular bioaccumulation

Transportation of metal across the fungal cell membrane is metabolism dependent which yields intracellular metal accumulation in viable cells [65]. The permeability of cell membrane greatly influences the uptake of cations following the steps such as: a) metal ion tends towards the outer cell surface, b) adheres to the inner cell surface, and c) transports into the cytoplasm [71]. Metal uptake occurs in two modes: (i) direct transport via carriers such as Na and K, which provides the sufficient energy required for the transportation [30], and (ii) indirect transport via ligands such as peptides, phosphates and amino acids, etc. The interaction of microorganisms with the metal ions differs with the type of metal transporting into the cytoplasm across the cell membrane. Accumulation, precipitation, redox and metabolic by-pass are few reported mechanisms that are independent of metabolic activity that is frequently associated with fungi's active defense mechanism [72, 73, 74].

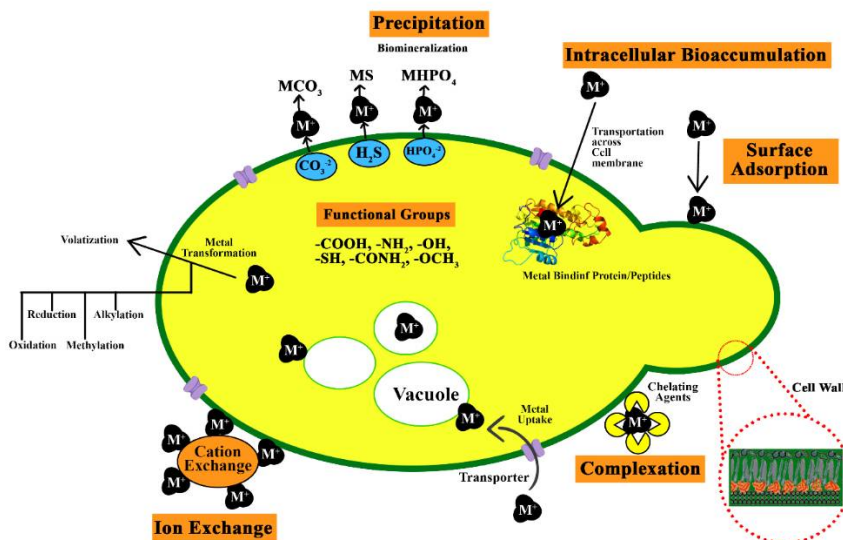


Figure 1. Schematic representation of Biosorption mechanisms showing fungal cell- metal interactions.

Metal ions that enter the cell are segregated into various organelles such as mitochondria and vacuoles [75]. Metal ions such as Co, Cu, Zn, Cd, and Hg readily activate the metallothioneins (MT), which are cysteine-rich and possess a good metal binding property [76]. By contrast to metallothioneins, phytochelutins, glutathiones (GSH) and some other cellular thiols have also displayed higher sensitivity to toxic metal ions [63,77]. The biosorption of copper by *Aspergillus niger* was found to be mainly because of metabolically active process that results in bioaccumulation [71]. Involvement of many genes in the tolerance and detoxification of metals have been reported. The yeast, *S. cerevisiae* exhibited the tolerance against Cu, Co, Cr and As. Modifications of cell surface by genetic tools influence the metal adsorption efficiency of the biomaterial. Cell surface-engineered *S. cerevisiae* produce histidine hexapeptide that can initiate better uptake of copper and shows enhanced self-accumulating properties [78, 79, 80]. Fungal vacuoles can regulate the cytosolic metal ion concentrations and also contributes in the adsorption and detoxification of metal ions. The investigation by Ramsay and Gadd confirmed that the mutants of *Saccharomyces cerevisiae* defective in vacuolar function exhibited higher sensitivity and lower adsorption capacity for the metals such as Zn, Mn, Co, and Ni [81].

Cell surface sorption/ precipitation

Physical adsorption

Physical adsorption is caused by non-specific force of attraction similar to van der Waals' force, which is both rapid and reversible [82]. Metal ions are transported from liquid to solid phase in three main steps that includes: (i) transfer of ion across the liquid layer of the particle; (ii) transfer happening within the particle boundary; and (iii) adsorption onto the external surface and later into the particle [83]. Electrostatic adsorption, on the other hand, is caused by coulombic forces of attraction among the charged solute and the adsorbing phase of biomaterial [84, 85, 86]. The biosorption of metals like cadmium, copper, and cobalt by dead biomasses of algae, fungus, and yeasts is thought to occur via electrostatic interactions between metal ions in aqueous solutions and microbial cell walls [87,88]. Electrostatic interactions have been shown to be responsible for chromium biosorption onto *Ganoderma* and *Aspergillus* species [19].

Ion Exchange

Ion exchange is the phenomenon in which the adsorbent release ions as a substitute when it comes in contact with an oppositely charged ion of the ligands that is present on the cell wall [89]. This technology cannot be applied on a wider scale since it is more expensive and can be primarily used to remediate the water effluents with lower concentration of heavy metals [17]. The concept of ion exchange as a significant method in bio sorption involves a range of physical (electrostatic or van der Waals forces) and chemical binding (ionic or covalent bonding) [90, 91]. The cell walls of microorganisms are rich in polysaccharides to which bivalent metal ions interact with their counterions [87]. The protonated form of amine groups which is cationic becomes neutral when deprotonated. Phosphate and carboxyl groups that are neutral on the other hand acquires negative charge if deprotonated. The relationship between electrostatic attraction and biosorption is defined by the type and the number of functional sites present in the sorbent, as well as based on the charges occupied, which is determined by the pH and pKa values of the corresponding group [92]. Tobin et al. showed the uptake of various heavy metal cations such Mn^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} , Pb^{+2} , Hg^{+2}

due to the presence of carboxylate and phosphate groups on *Rhizopus arrhizus* biomass. Whereas, the adsorption of molybdate and vanadate anions is found to be pH dependent, this occurs due to the strong electrostatic attraction towards the positively charged functional groups [64].

Furthermore, the removal of selected ions from multi-metal systems (such as industrial and sewage effluent) remains unaffected in the presence of competing metal ions. Biosorption of copper (89-100%) onto the fungus *Ganoderma lucidum* was facilitated via ion-exchange process [93]. The heavy metals like Pb(II) and Cd(II) are showed to be accumulated onto *L. scrobiculatus*, *A. rubescens* due to the availability of more active sites and exchanging ions [94, 95]. Higher dosage of *Pleurotus platypus*, *Agaricus bisporus* and *Calocybe indica* resulted in better removal of heavy metals such as Pb(II) and Cd(II) [96]. The SEM paired with an X-ray dispersion analyzer revealed that Pb⁺² exchanged K⁺ and Ca⁺ on *Mucor rouxii*, indicating ion exchange as one of the key mechanisms for the biosorption of metal species onto the fungal strain. Both the species of *Aspergillus* and *Mucor* have biological polymers (chitin and chitosan) on their cell walls, which provide eminent metal chelating ability [97]. Similarly, Ghasemi et al. demonstrated the subsequent release of hydrogen ion during the adsorption of metal at a controlled pH [98].

Complexation

Complexation is significant process that mediates the formation of a complex on the cell surface which mediates the removal of metal from the solution through the transition between sorbent-sorbate and metal-ligand interactions [70]. The number of ligands that a central atom carries in a complex is called coordination number. The complex formed when one ligand is attached to central atoms via two or more coordinated atoms is known as chelate [92]. The complex is constructed in such a way that neutral or anionic ligands usually surround the cationic central atoms. Such ligands are found to be present in the different functional groups of the fungus which includes the amino, phosphate, and hydroxy-carboxyl, which engage with metal ions in a systematic manner [69, 99].

Some fungi can synthesize organic acids, such as fumaric, malic and citric acids, which could chelate harmful heavy metals and lead to the development of organo-metallic complexes [17]. These acids facilitate the solubilization of metal complexes and metal leaching from their surfaces. Carboxyl groups present in polysaccharides and polymers of microorganisms involves in the biosorption or complexation of metals [19]. Heavy metal binding to biosorbents with diverse functional groups is influenced by ionic characteristics such as electronegativity, redox and ionization potential. It was shown that the removal of copper can be possible by the development of insoluble complexes between Cu²⁺ and anionic species like OH⁻, CO₃²⁻, and SO₄²⁻ on biosorbent surface [100].

Extra cellular accumulation/ precipitation

Precipitation can be dependent or independent of metabolic activities, which means that metal uptake can occur both in the aqueous solution and on the cell surface [13, 17]. Metal removal from aqueous solution is often linked with an active defense system of microorganisms, which react in the presence of toxic metal generating chemicals, enabling precipitation. The chemical interaction in a cellular metabolism-independent precipitation may occur between the metal and the cell surface [17]. It is widely accepted that a combination of various mechanisms, each operating independently, can contribute to overall metal uptake.

Few microorganisms produce extracellular polymeric substances (EPS) such as glycoprotein, lipopolysaccharides, peptides, etc. that are having considerable amount of anionic active groups and can biosorb toxic metal ions [101]. According to the few published studies, metal biosorption using EPS mainly focuses on *Bacillus* sp., *Pseudomonas* sp., sulfate-reducing bacteria (SRB), Cyanobacteria; however, EPS studies on fungus are limited with scarce information. Though few studies demonstrated the metal biosorption activity of the EPS secreted by the *Bacillus* sp., *Pseudomonas* sp., sulfate-reducing bacteria (SRB), Cyanobacteria, very few studies are available with the fungal EPS [102, 103]. In *S. cerevisiae*, the lead uptake by living cells is less than dead cells, whereas in *A. pullans* the lead uptake is greater in living cells. This could be because of extracellular polymeric substances secreted by the live *A. pullulans* [104].

Table 2: Various factors affecting the removal Efficiency and adsorption capacity of fungal species in contaminated water system.

Fungal Species	Source of Isolation	Modifications	Heavy metal	Contact time	initial Temp	Initial pH	Initial metal ion concentration	Biosorbent dosage	Removal Efficiency (%) / adsorption capacity (mg/g)	References
<i>Aspergillus flavus</i> strain KRP1	orest soil	-	Hg	-	-	4.13	10mg/L	14.9g/L	97.50%	[202]
<i>Aspergillus fumigatus</i>	-	Live Dead	Pb Cd Pb Cd	4-5h	28 °C	5	250 and 10mg/L	150mg/L and 0.4mg/L	21.57mg/g 6.286mg/g 3.65mg/g 0.83mg/g	[230]
<i>Aspergillus niger</i>	Polluted air in a fuel station	Iron oxide coated	Cu Ag Co Hg Zn	24h	28 °C	5.5	100mg/L	1g/L	37% 48% 71.4% 83.2% 100%	[231]
<i>Aspergillus niger</i>	-	Alkaline treated	Hg	2h	40 °C	3	250mg/L	0.8g/L	40.53mg/g	[156]
<i>Aspergillus niger</i>	-	-	Cr	158 h	35-45 °C	2	50mg/l	10g/L	-	[60]
<i>Aspergillus tubingensis</i> Merv4	Plant sample	Dead Biomass	Zn Hg	12-24h	30-35 °C	5.5	200mg/L	0.2g/L	96% 91 %	[232]
<i>Aspergillus versicolor</i>	-	-	Hg	24h	30 °C	6	20mg/L	4g/L	75.6mg/g - >95%	[126]
<i>Candida albicans</i>	River water	Iron-oxide coated	Zn Cu Hg Co As Cd Ag Pb Cr	24h	28 °C	5.5	100mg/L	1g/L	22% 31% 36% 37% 40% 46% 51% 57% 76%	[233]
<i>Candida parapsilosis</i>	Industrial wastewater	-	Hg	-	-	-	-	-	80%	[234]
<i>Ceriporia lacerata</i>	litter of invasive plant	-	Cu	2h	25 °C	6	100mg/L	2g/L	6.79mg/g	[61]
<i>Cladosporium halotolerans</i>	gold mine area	-	Hg	-	-	-	100mg/L	-	90.72%	[235]
<i>Didymella glomerata</i>	Rhizosphere soil samples	-	Hg	2days	-	-	100mg/L	-	97%	[236]
<i>Dendryphiella salina</i>	Sea water	-	Hg	2days	RT	-	36.94	20µL	80-92%	[237]
<i>Funalia trogii</i>	-	Live Dead	Hg Cd Zn Hg Cd Zn	1h	20 °C	6	500mg/L	-	333mg/g 164.8mg/g 42.1mg/g 403.2mg/g 191.6mg/g 54mg/g	[208]
<i>Mucor rouxii</i> IM-80	Leather works	-	Hg	24h	30 °C	5.5	100mg/L	10g/L	95.30%	[127]
<i>Penicillium canescens</i>	-	-	As Hg Cd Pb	4h	20 °C	5	500mg/L	1g/L	26.4mg/g 54.8mg/g 102.7mg/g 213.2 mg/g	[107]
<i>Penicillium purpurogenum</i>	Soil	-	As Hg Cd	4h	20 °C	5	100mg/L	1g/L	35.6mg/g, 70.4mg/g,	[118]

			Pb						110.4 mg/g, 252.8mg/g	
<i>Phanerochaete chrysosporium</i>	-	Live Dead	Hg	1h	20 °C	6	200mg /L	-	83.10mg/g 102.15mg/g	[238]
<i>Pleurotus eryngii</i>	-	-	Hg	5mi n	30 C	7	7.5mg /L	0.25g/L	34.01mg/g 98.7%	[115]
<i>Pleurotus ostreatus</i>	-	Live Dead	Cr	360 h 22m ins	28 °C	5.6	25mg /L	50mg/L	169.84mg/g -100% 368.21mg/g -100%	[69]
<i>Pleurotus ostreatus</i>	-	Dead	Cd	10m in	26 °C	6	10mg /L	0.5g/L	-	[239]
<i>Pleurotus sajur-caju</i>	-	Live Dead	Hg	1h	20 °C	5.5	200mg /L	-	81%	[240]
<i>Polyporus squamosus</i>	-	-	Hg	4h	20 °C	5.3	47.39mg /L	-	3.54mg/g - 35.37%	[241]
<i>Rhizopus arrhizus</i>	-	live Dead	Ni	6h	25 °C	6	100mg /L	0.5mg/L	169.8mg/g 368.2 mg/g	[242]
<i>Rhizopus cohnii</i>	-	-	Cd	2h	-	4.5	100mg /l	1g/L	40.5mg/g - 80%	[58]
<i>Rhizopus Oligosporus</i>	corn processing wastewater	-	Hg	6h	30 °C	6	100mg /L	1g/L	33.33mg/g	[119]
<i>Saccharomyces cerevisiae</i>	-	Magnetic ally modified	Hg	1.5h	35 °C	5	200mg /L	1g/L	114.6mg/g	[113]
<i>Streptomyces ciscaucasicus</i>		Live Dead	Zn	8h	28 °C	5	150mg /L	2000mg/L	42.75mg/g 54mg/g	[243]
<i>Tolypocladium sp. -Mycelium Sterilae MS 2929</i>	Industrial waste	Methano l treated	Hg	3day s	-	7	-	-	161mg/g	[244]
<i>Trametes versicolor</i>	-	Live Dead	Cd	1h	25 °C	5.5	600mg /L	25mg/L	102.3mg/g 120.6mg/g	[245]

FACTORS INFLUENCING IN FUNGAL BIO-SORPTION EFFICIENCY

Contact time

The dispersion of metal ions between solution and sorbent are affected by the contact time. The bio sorption rate was found to be rapid (90%) in the initial period (within an hour) due to the availability of free active sites. But as the time increases, the efficiency of biosorption decreases due to the increase in the concentration of saturated metal ions [105]. The rapid biosorption was observed for Pb(II) by dead biomasses of *Rhizopus sp.* and *Aspergillus niger* in 1hr with greater biosorption efficiencies of 9.21 and 8.94 mg/g biomass respectively [106]. The equilibrium period varies with physical properties of sorbent material such as pore size distribution, morphology, and charge density etc. Adsorption equilibrium might also be influenced by factors such as adsorbent dose, metal ion concentration, and the concentration of competing metal ions [107].

Among yeast, molds and mushrooms, filamentous fungi are found to be more utile in the metal remediation from liquid media than any other species [106, 108, 109]. *Aspergillus niger* exhibited strong resistance to heavy metals such as Cu, Cd, Ni and was also found to be efficient in removing Cr up to 60% [25]. The study on filamentous fungi, *Trichoderma sp.* revealed the uptake of Zn, Cd, Pb, Cu, and Ar [110, 111]. Several yeast species such as *Candida albicans*, *Saccharomyces cerevisiae*, *Candida tropicalis* etc. are egressed as a good biosorbents due to the presence of glycoprotein and their involvement in bioremoval [112]. *Saccharomyces cerevisiae* can remove up to 114.5mg of Hg /g of biomass within 90min [113] and induce the uptake of 60% uranium in 15min of contact [108]. da Rocha et al. studied the efficiency of the mushroom,

Pleurotostreatus in the adsorption of Cr metal and the study noticed the uptake of 100% Pb from polluted water [114]. *Pleurotus eryngii* showed 98% of Hg uptake within 5min of contact time, whereas the efficiency of *Pleurotus eous* was recorded to be around 93.2% for Pb [115, 116]. The equilibrium period required for the adsorption of mercury on immobilised carboxymethylcellulose by *Phanerochaete chrysosporium* was approximately 1 hour [117], *Penicillium purpurogenum* attained equilibrium state for metal adsorption by 4h [118]. Equilibrium time for bioremoval of Hg vary between different species. Immobilized *Pleurotus sapidus* exhibited equilibrium for bioremoval at 1hr [117], whereas it was determined to be 6h for *Rhizopus oligosporus* [119]. Ozsoy and van reported the biosorption capacity of dried *Rhizopus oligosporus* biomass for Ni (II) ions during the first 6h. Say et al. investigated the application of the fungus *Penicillium canescens* in the removal of lead, mercury and cadmium metal ions in 4 h [120].

Optimum temperature

The temperature of sorption medium is an important parameter that mediate the bioremoval of metal ions. Temperature influences the energy-dependent mechanism of metal adsorption within the range of 20-35°C [62]. Temperature also influences integrity of cell membrane, conformation, and oxidation/ reduction of chemical compounds. Temperature fluctuations alters the process of metal removal since it is primarily dependent on the physiochemical properties of the medium [121]. The kinetic energy and surface activities of the solute increases at higher temperatures resulting in the enhancement of biosorption. However, it has been discovered that increasing the temperature reduces the biosorption ability of the biomass and causes extracellular damage to the biosorbent. Low temperature, on the other hand, has an effect on live cell systems and influences the auxiliary metabolism-dependent mechanisms that facilitate biosorption [19]. The maximum Ni and Pb bioremoval by *S. cerevisiae* was attained at 25 °C and was observed to decrease when the temperature was raised to 40 °C [122]. *Aspergillus versicolor* recorded significant removal of Fe with maximum of 22.2 mg/g at 31°C [121]. The study on Hg(II) removal efficiency by *Pleurotus eryngii* determined as 98.7% at 30°C that further decreased to 90.42, 85.4 and 80.5% with increasing temperatures of 40, 50 and 60°C respectively [115]. Two strains of *Aspergillus sp.* (*Aspergillus fumigatus* RH05 and *Aspergillus flavus* RH07) showed maximum Zn uptake at 28°C [123]. The bioremoval of Cu (II) using *Aspergillus flavus* was 40.8% at an optimal temperature of 26°C while for Pb removal (45.5%) by *Aspergillus niger*, the optimal temperature was 37°C [124]. The maximum biosorption efficiency of *Alternaria alternata* and *Penicillium aurantiogriseum* for cadmium and mercury was achieved at the temperature of 30°C [125]. Unfavourable Hg(II) sorption by *Aspergillus versicolor* and *Rhizopus oligosporus* was noticed at higher temperature [119, 126]. Exothermic Hg(II) removal by *Mucor rouxii* IM-80 showed the maximum removal upto 95.3% at 30°C which decreased to 71.4% at 40°C [127]. *Trichoderma* fungus exhibited better biosorption rate for Pb ions of about 98.8% at 25 °C which occurs after 120 mins of contact time [128]. Dead biomass of *Aspergillus terreus* exhibited maximum biosorption of Cr(VI) at 27 °C [129]. El Maghrabi et al. revealed that the rate of biosorption of Mn on *Aspergillus versicolor* was maximum at 90ppm concentration within 15 mins at 31 °C [130].

Optimum pH

pH remains as a vital factor in influencing the biosorptive process by affecting chemistry of metal solution, metallic ion competition, ligand activities in biomass, and in the activation of cell surface binding sites [115, 131, 132]. At lower pH levels (pH < 5), binding sites especially amine/amino and carbonyl groups would be more readily protonated in close association with the hydronium ions, resulting in a weaker affinity with Hg(II) ion because of the repulsive forces which in turn increases the competition between H₃O⁺ ions and metal ions in the solution. At higher pH levels (pH > 5), binding sites become more active by carrying negative charges, thus the metal ions with a positive charge are easily adsorbed on cell surface with subsequent attraction [133]. Adsorption tests performed at pH more than 7.0, showed increased precipitation or hydroxide formation with metal ions due to excess of ions in the solution [134].

According to Soleimani et al., removal of cadmium using *Aspergillus versicolor* increased with the decrease in pH. Cadmium uptake was shown to be maximum at pH 4.0 for both live and dead biomass, and at pH 6.0 for dried biomass [135]. The effect of pH on biosorption of mercuric ions was investigated using various fungal biomasses. Maximum adsorption efficiency was achieved at pH range of 5.0-7.0 by *R. oligosporus* [119], *penicillium canescens* [107], *P. eryngii* [115], *A. versicolor* [126]. At a pH of 5.0, the dead biomass of *Trichoderma sp.* BSCR02 showed maximum adsorption efficiency of 82.3% for chromium at 35°C with 200mg/l of metal ion concentration [136]. Whereas, maximum biosorption of cadmium and mercury using *Alternaria alternata* and *Penicillium aurantiogriseum* was depicted at pH 6.0. As a result, the optimal pH for maximum Hg(II) sorption was determined to be between 5.0 and 6.0. [125] or around 7.0 [40]. The biosorption capacity of *Penicillium sp.* for Pb is highly sensitive and was found to be directly proportional to pH. Maximum bioremoval was determined at pH 5.5 for both dry and wet biomass [128]. Whereas, at pH 4.0, the maximum removal values of Pb(II) and Ni(II) for *Penicillium sp.* were 47% and 76% with a contact time of 65 and 89 mins respectively [137]. The bioremoval capacity of *Aspergillus fumigatus* for cadmium

was better up to pH 5.0 and then gradually decreased with further rise in pH [138, 139]. *Fusarium sp.* showed potential adsorption of Zinc for dead biomass (62.0%) than live biomass (42.3%) at pH 6.0 [140]. The zinc removal by live and growing strains of *A. fumigatus* and *A. flavus* differs with variations in pH i.e., optimal pH for growth and bioremoval of metal ions in both strains were 5.0 and 4.0, respectively [123].

Metal ion concentration

The metal ion concentration plays an important role as a dynamic force to establish sorption between solid and liquid media [141]. The fungal cell walls have a negative charge due to the arrangement of metal binding groups, which includes the amino, sulphate, carboxyl, and phosphate groups. Phosphate-containing teichoic acid in the fungal cell wall is predominantly responsible for metal binding [142]. Soft metal form more stable bonds with nitrogen or sulphur-containing (soft) ligands [143]. The biosorption capacity of biomass increase initially with the increase in metal ion concentration and further reaches a plateau value, indicating the saturation of available active sites on the adsorbent surface. Further increment of metal concentration decreases the percentage of adsorption due to unavailability of free binding sites.

The maximum adsorption capabilities of *Penicillium canescens* dry fungal biomass was 102.7 mg/g for Cd(II), and 213.2 mg/g for Pb (II) [107]. Biosorption capacities of the *M. rouxii* IM-80 strain for the Hg (II) ions was assessed at a concentration ranging between 100 and 500 mg/L [127]. The magnetically modified yeast cell's capacity for mercury (II) biosorption was initially higher until an equilibrium concentration of Hg²⁺ was attained and further a plateau value of 150 mg/L with a maximum biosorption of 114.6 mg/g was observed [113]. These results may be due to the competition among the number of metal ions to bind free active sites or due to the lack of active sites on the surface of biomass at higher metal concentrations [144]. The efficiency declines after reaching the optimum concentration level due to an increase in metal dose beyond the toxicity level that fungus gets damaged [136]. Sorption capacity of *Beauveria bassiana* increased to 13.5 mg/g for cadmium, 12.2 mg/g for copper and zinc, and 11.3 mg/g for chromium with the increase in the initial metal ion concentration of 100 mg/L [145]. Whereas, the sorption capacity of *Aspergillus versicolor* isolate was about 43.6 mg/g and 51.9mg/g for Cu (II) and Pb (II) respectively at an initial metal concentration of 300mg/L [146] which is less than the results obtained by *Fusarium solani* [147] but more than that obtained by *Aspergillus niger* [148]. Similar trend was shown by El-Sayed with live and dead biomasses of *Aspergillus awamori*, where maximum cadmium uptake capacity was observed at an initial metal ion concentration of about 500mg/L with 1g/L of biosorbent dosage [149].

Biosorbent dosage

The adsorbent dosage strongly influences the extent and percentage of biosorption. In most of the cases, higher metal uptake occurs when biosorbent dose is low. Generally, the biosorption of solute increases with an increase in the concentration of biomass, due to the availability of more exchangeable sites by the enhancement in the surface area of biosorbent [150]. But the interference between the active binding sites cannot be reversed, as it depends on the uptake capacity of the sorbent [72]. Similarly, the increase in the concentration of *R. arrhizus* biomass (from 0.15g/L to 0.50g/L) resulted in increased uptake of copper (29.83mg) at the concentration of 30mg/L [151]. However, the higher concentration of biomass showed rapid adsorption by producing more concentration of the cell than the metal in the solution. The percentage of lead removal increased to 52.5%, 59.5%, and 66.5% with the increasing cell mass for *Aspergillus flavus* HF5, *Aspergillus sp.* RBSS-303, and *Aspergillus caespitosus* respectively at 0.75g of biosorbent dosage/L of lead solution [152]. Argun et al. correlated the parallel tendency of adsorption efficiency and adsorbent dose due to the increasing surface area of unbounded sites [153].

The increase in sorbent dosage of macrofungus, *Ganoderma carnosum* from 0.2 to 4.0 g/L resulted in the rapid increase in the bio-removal of Pb (II) ions from 5.6% to 75.16% [154]. Bioremoval of Pb(II) may be due to the increase in the availability of more active sites for the complexation of heavy metal ions [155]. Increase in sorbent dosage does not lead to a significant improvement in biosorption capacity after the attainment of equilibrium. Further metal uptake and the reduction rate declined as biosorbent dosage increased. When the sorbent dose was increased from 0.8 to 16.0 g/L, Hg absorption capacity of *Aspergillus niger* decreased from 21.8 to 2.7 mg/g [156]. Beebi et al. indicated that the biosorption efficiency of dry fungal biomass is elevated even at high metal ion concentration in which percentage removal of nickel and copper for the initial concentration of 20ppm and 100ppm are 75.5 to 71% and 55.5 to 50% respectively [157]. Similarly, Mahmoud et al. revealed noticeable elevation in the removal efficiency for Al, Fe and Mn using 3g of dried biomass of *Aspergillus oryzae* upto 71.9, 69, and 58% respectively [158]. 2.5g of *Aspergillus flavus* dead biomass have maximum chromium removal efficiency of about 92%, while increasing the adsorbent dosage had no effect on adsorption [159]. The biosorption of Nickel by dried *Rhizopus oligosporus* was analyzed for various biosorbent doses ranging from 0.5 to 5g/l, and it was reported that the biosorption efficiency declines as the biosorbent dosage increases which might be due to the aggregation of biosorbent particles that may inhibit the sorption process [160].

PROBLEMS CONSOCIATED WITH FUNGAL BIOSORPTION TECHNOLOGY AND SUITABLE REMEDIES

Exhausted bio-adsorbents and metal ions

The fate of exhausted bio-adsorbents obtained during the elution process is the fundamental issue resulting from the biotechnological use of biosorbents in the remediation of toxic pollutants. Measures need to be adopted in such a way that fixing one problem should not result in the emergence of a new one [161]. Issues related with safe disposal of exhausted sorbent materials and recovery of the solute from metal ion loaded solutions are to be addressed.

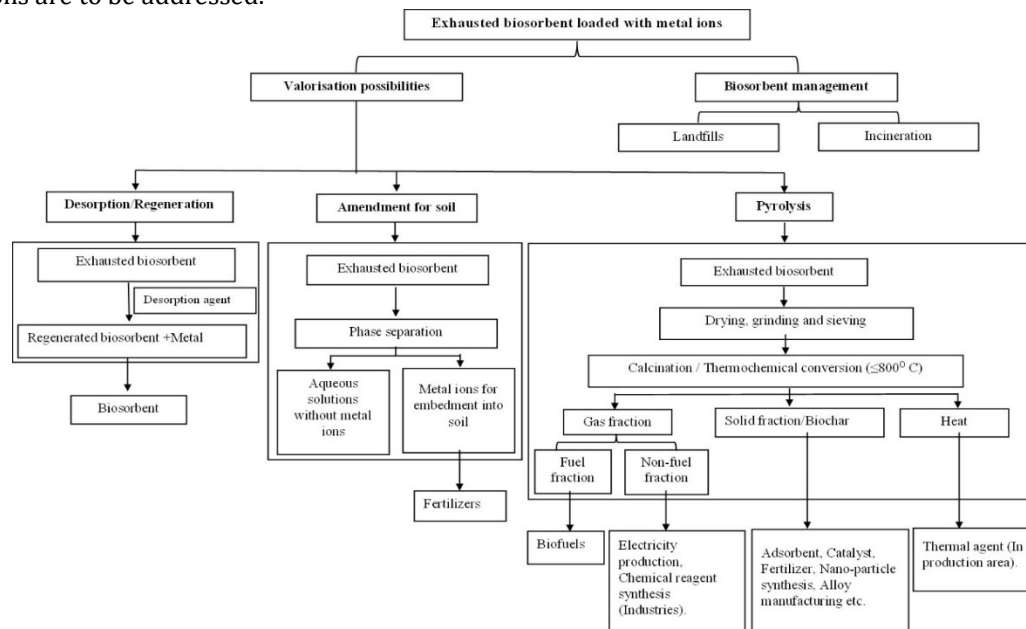


Figure 2. Flow chart showing the valorisation and management possibilities of exhausted biosorbent loaded with metal ions.

Though metal loaded biomaterial can be disposed through landfills or incineration; landfill is gaining less attention as it may cause groundwater contamination. Whereas incineration is limited only to non-immobilized biomaterial since biomass immobilized in a polymeric matrix is non-viable. The recovery of solute can be carried out by the process such as electroextraction. It was evidenced that use of electrowinning/ electroextraction process is often feasible for the metal recovery from concentrated metal solutions [162]. Moreover, microbial biomasses originated from the industries not only polluting the environment but also lead to the loss of economy. For example, the fungal wastes generated after industrial production of fruiting bodies from *Ganoderma lucidum* showed the removal efficiency of about 87% and 84% for Pb(II) and Cd(II) respectively [163]. If the biomass is inexpensive or if processing and transportation costs are low, the use of metal rich adsorbent materials to absorb other solutes can be easily achieved. Biosorption experiment on molybdate-loaded chitosan beads showed that molybdate's chelating affinity can be employed to recover As(V) from aqueous systems [164]. Like this, the generated biosorbent wastes could serve its purpose by being reused to mitigate their own damage by giving worth to their disposed wastes in order to fulfil goals of a circular economy. Utilization of waste fungal biomasses in the process of metal removal will reduce the problems caused by the pollutants in the environmental protection, and provide a potential method of valorization.

Valorization possibilities of exhausted biosorbents

The biosorbents saturated with heavy metals after adsorption are examined from both biotechnological and ecological standpoint, in order to overcome several obstacles of exhausted biosorbents. The need to strengthen the pertinency of sorption on a broader scale before employment of biosorbents to treat industrial effluent is rising [165]. Recent researches have shown few possible measures for valorization of metal loaded biosorbents, such as: recovery and recycling of sorbent material, utilization of saturated metal loaded biomaterials as soil fertilizers for the lands deficient in key microelements, and pyrolysis of biomaterial in proper circumstances [161].

The most acceptable method in the valorization of exhausted metal ions is the regeneration of sorbents by desorption, which in turn can be reapplicable in industrial activities and adsorption cycles [161]. The desorption of ions is possible when desorption agents with suitable experimental conditions are used in the treatment of exhausted biosorbents. Adsorbed ions are substituted by other ions from the agents. H_2SO_4 ,

HCl, KNO₃, CaCl₂, EDTA etc. have been used as the desorption agents [166, 167, 168, 169, 170, and 171]. The efficient desorption method must be modelled in such a way that, optimum pH of biosorption should be different with the pH of desorption agent in order to facilitate the shift in the elementary equilibrium. The amount of exhausted biomaterial must be higher than the volume of desorptive agent solution to minimize the cost. The process must be optimized at ambient temperature considering the economic importance in process development for industrial biosorption [161]. Even though, this process has many advantages like, easy recovery, simple method of regeneration, low operating cost, it also faced a major drawback due to less rigid and declining properties of biosorbent which became the main reason that hinders the wide applicability of desorption [172, 173]. Sorbents disposed by incineration or landfills have serious ecological implications that may lead to higher toxicity [174, 175, 176] In order to improve the ecological quality of biosorption, more valorization solutions for treating exhausted biosorbents must be investigated [175].

Considering the main advantages of biosorption process, the exhausted biomasses shall be used in agriculture as an alternate fertilizer to improve the soil quality. Valorization possibilities interfere with the significant amount of metal ions retained in biomasses and also influence the regeneration of biosorbents [177]. Release of the retained metal ion which are rich in macronutrients such as N, P, Ca in the biomass reach the soil and enhance fertility [178, 179, 180]. But unfortunately, all the saturated biomasses cannot be used as soil fertilizers, as it should meet some conditions. Chemical composition of treated industrial effluents must be simple and well-known, the biomasses used in biosorption must be easily degradable and must not be a source of soil pollutant [180, 181]. In order to vindicate all these conditions, huge amount of exhausted biomasses resulted from industries are often used in soil nourishment and such biomass are less expensive due to its huge availability [181, 182]. The washing waters treated in the depositions baths after metallic coatings (Cu(II), Zn(II), Ni(II) plating) have high concentrations of given metal ion with low level of toxic ions or organic compounds [183, 184]. This may have some advantages: provide safe metal ions with role of microelements (non-toxic) and thereafter the metal removal from their surface, washing water can be recycled which are beneficial for environmental sustainability [182, 183, 184]. In case of agricultural and wood biomasses, the cellulose and hemicellulose content are high which requires longer time in degradation. Such biomasses could be used in moist soil, where desorption liberates metal ions into the soil and slow degradation of biomass improves air circulation and hydrological properties [185, 186, 187]. Even though the exhausted biosorbent have many agricultural benefits in solving inadequacies related to biosorbents regeneration, this valorization has a few limitations: solely non-toxic metals from some industrial effluents., uncontrolled release of metal ions into soil from the surface of biosorbent [188], requires huge quantity of exhausted biomass for soil treatment due to the presence of low content of nutrients and essential microelements. Therefore, other valorization possibilities should be explored to achieve sustainable environment.

The thermochemical conversion (pyrolysis) is the most accepted method of valorization, due to its economically viable and easily adaptive nature [189]. Even though, it was considered as a good method for reducing wastes and limits landfills, current research investigations have shown that pyrolysis of biomass done under well-defined circumstances can be transformed into more economically valuable value-added goods [190]. During pyrolysis, following bio sorption, the exhausted biomass is dried and ground before being subjected to a thermochemical conversion at a specific temperature (not exceeding 800°C) that is suitable for a particular biomass [191]. The products of pyrolysis such as biomass, biochar and heat produced after the pyrolysis can be individually victimized [190, 191, 192, 193 and 194]. The solid residue/biochar resulted from the pyrolysis have more applications in soil amendment, nanoparticle synthesis, additives and in alloy manufacturing, etc. [195, 196, 197 and 198]. The pyrolysis of biomass wastes explores more significant advantages compared to the other two valorization possibilities, as it can be utilized for all forms of exhausted biomasses (both toxic and non-toxic) and can be easily applicable in large industrial sectors due to its simple operating steps (drying and grinding). Although, the products resulted after pyrolysis have high economical worth that greatly aid in the betterment of process. Few drawbacks such as the requirement of high capital investment (for equipments, instruments etc.) for the implementation of process, more attention for technological installations during large scale operations in order to achieve environmental sustainability, presence of toxic metal species (organic and inorganic compounds) in the final biproducts(biochar) obtained after pyrolysis are to be still addressed.

SUCCEEDING DIRECTIONS AND CHALLENGES FOR RESEARCH ON FUNGAL BIO-ADSORBENTS

Although the development of biosorption and its tools are optimized in a larger extent, the industrial applications are still limited. The major reason behind this limitation might be due to the failures or poor understandings about the mechanisms of biosorption technology. The present drawbacks and advancements in this field can be treated with fungal biomaterials. For decades, fungi have been considered

as an economically feasible promising biomaterial for bioremediation of toxic metal pollutants from wastewater effluents due to their unique features. Challenges in formulating fungal bio sorption largely depends on the factors such as (i) identification and selection of novel potential biosorbents (ii) construction of biosorption models for industrial applications (iii) scaling up of effective biosorption process at varying environments (iv) scaling down the assessment costs for biosorbent in market (v) introduction of molecular tools to enhance the rate of biosorption by the construction of genetically modified organisms. Identification of eco-friendly approach also should pick up a low-cost biomaterial and a suitable immobilization technique [199]. Implementation of novel tools, and enhancement of immobilized biosorbent properties such as porosity, and, surface integrity are important factors that needs to be further refined. The use of hybrid technologies has become the major solution to the existing problem, in which several processes are combined to achieve the target of absorption at the commercial scale. Methods such as intra-biotechnological (bio-sorption, bio-reduction and bio-precipitation) or inter-biotechnological (chemical precipitation, electrochemical processes etc.) is receiving wide applications in the metal removal. To attract biosorbent technology, specific strategies for accepting the saturated biomaterial must be formulated, where the biosorbent can be further processed. Renewal and desorption of biomass or to transform the recovered metals into a usable value-added product are major challenges. Developing strategies involving a multidisciplinary approach that combines technological and fundamental sorption sciences provide innovative technology in metal sequestration. Major drawbacks such as inefficient metal remediation tools, usage of more chemical reagent, high energy requirements, toxic sludge or wastes production with disposal challenges, have often become the fundamental contentions to support biological approach to offer potential solutions to the remarkable problems caused by metal toxicity.

CONCLUSION

The present review illustrates several successful examples of biosorbents developed from different biomasses and their practical applications in the removal and recovery of heavy metals. The fungal biomass used as bio-adsorbents for heavy metal sequestration are cost-effective and are reported to be a beneficial alternative for the existing commercial adsorbents. The mechanisms and adsorptive properties of fungal adsorbents are discussed. Though few literatures have been reported on the removal efficiency of fungal adsorbents. Yet, less attention has been given to this field of research towards solving industrial needs. Future perspectives might focus in the removing properties of bio-adsorbents by enhancing modification tools (acid, alkali/base, and thermal treatment), desorption mechanisms and regeneration of adsorbents, recovery of metal ions. Aside from biosorption, the other properties of microorganisms and their interactions with other microorganisms that are part of metal complexation, metal transformation, metal reduction, metal crystallization, metals binding with proteins and metal dissolution should be assessed at the large scale. The use of hybrid biological advancements such are bioleaching, biofloatation and bioreduction should also be measured for metal recovery from wastewater.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

AUTHORS CONTRIBUTION

Vinanthi Rajalakshmi K S has contributed in compiling of the theoretical data and manuscript preparation. Paari K A. and Rajesh Rajendran have contributed towards the designing of ideas that has helped in the formation of this manuscript.

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DATA AVAILABILITY

The reference articles and other sources of information that has been used in this review article has been collected from the google scholar and other scientific community websites.

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