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ORIGINAL PAPER

Ecotoxic heavy metals transformation by bacteria and fungi in aquatic ecosystem

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Abstract Water is the most important and vital molecule of our planet and covers 75 % of earth surface. But it is getting polluted due to high industrial growth. The heavy metals produced by industrial activities are recurrently added to it and considered as dangerous pollutants. Increasing concentration of toxic heavy metals (Pb^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}) in water is a severe threat for human. Heavy metal contaminated water is highly carcinogenic and poisonous at even relatively low concentrations. When they discharged in water bodies, they dissolve in the water and are distributed in the food chain. Bacteria and fungi are efficient microbes that frequently transform heavy metals and remove toxicity. The application of bacteria and fungi may offer cost benefit in water treatment plants for heavy metal transformation and directly related to public health and environmental safety issues. The heavy metals transformation rate in water is also dependent on the enzymatic capability of microorganisms. By transforming toxic heavy metals microbes sustain aquatic and terrestrial life. Therefore the application of microbiological biomass for heavy metal transformation and removal from aquatic ecosystem is highly significant and striking. This paper reviews the microbial transformation of heavy metal, microbe metal interaction and different approaches for microbial heavy metal remediation from water bodies.

Keywords Heavy metals · Ecotoxic · Microbes · Transformation · Remediation

Introduction

Bacteria and fungus are unique microorganisms that play a major role in the biotransformation of heavy metals. Water bodies contribute significantly for both aquatic as well as terrestrial life but they become polluted progressively due to mass development of industries and this is harmful for the surrounding life (Congeevaram et al. 2007). Municipal water and industrial waste discharge in water bodies damage the quality of water and affects the aquatic life. Due to globalization, increase in population and industrial development causes deposition of heavy metals in lakes and rivers. These are major issues that have been discussed by the developing and developed countries at world scenario (Souza and Tundisi 2003). Scientific approach may lead to solve these problems at in vitro to in vivo level as suggested by Hoppe (1993). A large number of populations were affected by mercury pollution in Minamata, Japan. It was caused by the release of mercury from chemical industry in Minamata Bay. This highly toxic mercury accumulated in the fish which was later eaten by the local population and resulted into mercury poisoning (Chang and Guo 2009). Loss of appetite, nausea, irritability, and muscular stiffness are common due to minor exposure of heavy metal to human. Prolonged exposure to different heavy metals such as cadmium, copper, lead, nickel and zinc can cause injurious effects on aquatic life as well as humans (Yan and Viraraghavan 2000). Despite the adverse

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effect of heavy metals, slight attention has been given for their presence in the aquatic ecosystem. Aquatic microorganisms especially bacteria and fungi secrete numerous amounts of extracellular enzymes that could efficiently do the transformation of heavy metal (Edwards et al. 2013). Bacteria and fungi transform heavy metals and make them available as micronutrients for the use of flora and fauna in water (Alexander 1994). This paper provides the emphasis on heavy metal effects on life and discusses the biotransformation of heavy metals specifically by bacteria and fungi in waste water so that there would be reduction of the heavy metal toxicity and concentration in aquatic ecosystem.

Heavy metal microbe interaction, equilibrium and kinetics

Biotransformation is the conversion of compounds by microorganisms through enzymatic reactions like oxidation, reduction and hydrolysis. It is the most vital process for the removal of the heavy metals from water, soil and sediment. Bacteria and fungus are good for removing heavy metal contamination of water naturally therefore biotechnologists have explained in vitro techniques to biotransform heavy metals using microorganism (Glazer and Nikaido 2007). Pollution from paper pulp, distillery, leather, petroleum, pesticide and beverage industries are the sources of heavy metals pollution but they can be remediated through microbial treatment (Thakur 2006). Fungi are also important for this purpose because they metabolize dissolved heavy metal from water bodies. Heavy metals can be precipitated as insoluble sulphides by the metabolic activity of sulphate reducing bacteria. Heavy metal ions can also be captured in the cellular organization of microbes and subsequently reduce the concentration. In the biosphere microorganisms transform carbon and play a symbiotic role to produce renewable energy and nutrient support for aquatic biodiversity (Park et al. 2010). In the same way microbial biomass helps to transform heavy metals by their food metabolism and make it available as nutrient in the food chain. Different heavy metals disposed in water and their regulatory limits (mg/l) as per Comprehensive Environmental Response Compensation and Liability Act (CERCLA), USA is summarized in Table 1.

Heavy metals can be transformed from one oxidation state to another by bacteria and fungi. They are also able to tolerate harmful effects of heavy metals. Metals (Cu^{2+}, Cd^{2+}, Pb^{2+} and Ca^{2+}) are recurrently found as soluble cationic forms. They are found as precipitates (CuS, PbS, and $CdCO_3$) in reduced conditions. Metal bioavailability increases at low pH (due to its free ionic metal species) and decreases at high pH (Rzymski et al. 2014). However, in contrast to other heavy metal bio availabilities, nickel form complexes with inorganic ligands (OH^-, SO_4^{2-}, Cl and NH_3) at wide pH range (5–9). The fate of heavy metals in water depends mainly on the initial concentration and some edaphic conditions such as pH (Katsoyiannis and Zouboulis 2004). Metal resistance mechanisms have been also identified in bacteria and fungi. Due to their strong ionic nature, heavy metals bind to many cellular ligands and displace native essential metals from their normal binding sites (Valls et al. 2000). Once metal binds with cell ligands, it is taken up by the microbes and transformation of toxic heavy metal starts. Microbes have the great ability to reduce the toxicity of the heavy metals or they convert insoluble toxic cations of heavy metals into less toxic soluble form. Archaea and Eubacteria are capable of oxidizing Mn(II), Fe(II), Co (III), AsO_2, SeO or decrease concentration of Mn(IV), Fe(III), Co (II), AsO_2^{4-}, SeO_3 and make them less or non toxic. Bacterial species (*Alcaligenes, Bacillus*, *Pseudominas*) do the reduction of Cr(VI) to Cr(III), reduction of Hg(II) to Hg(0), reduction of Se(VI) to elemental Se, reduction of U(VI) to U(IV). Several researcher showed that yeasts are also capable of accumulating heavy metals such as Cu(II), Ni(II), Co(II), Cd(II) and Mg(II) and are superior metal accumulators compared to certain bacteria (Rajkumar et al. 2012). Fungi are known to tolerate and detoxify heavy metals by active uptake, extracellular and intracellular precipitation and valence transformation. Many species of fungi can absorb some heavy metals (Cd, Cu, Hg, Pb, and Zn) into their mycelium and spores (Rajkumar et al. 2012). Cell surface functional groups of the fungus might act as ligands for

Table 1 Heavy metals and their regulatory limits (as per CERCLA, USA)

S. No.	Heavy metals	Maximum concentration limit (mg/l)
1.	Antimony (Sb)	0.006
2.	Arsenic (As)	0.01
3.	Cadmium (Cd)	0.005
4.	Chromium (Cr)	0.01
5.	Copper (Cu)	1.3
6.	Iron (Fe)	0.3
7.	Lead (Pb)	0.015
8.	Manganese (Mn)	0.05
9.	Mercury (Hg)	0.002
10.	Nickel (Ni)	0.2
11.	Radium (Ra)	5
12.	Selenium (Se)	0.05
13.	Silver (Ag)	0.05
14.	Thallium (Tl)	0.002
15.	Uranium (U)	30
16.	Zinc (Zn)	5.0

metal sequestration resulting in the removal of the metals (Pal et al. 2010). Many bacteria and fungi produce some cellular secretions that transform toxic metals from the food chain of aquatic ecosystem by being bound to the particular cellular secretions (Colberg et al. 1995). Microbes cannot degrade heavy metals directly but they can change the valence states of metals which may convert them into less toxic forms. Some reactions are explained below where microbes interact with metals and change the valency of heave metals that causes biotransformation/detoxification.

$$Mn(II) \xrightarrow[\text{Oxidation}]{\textit{Eubacteria}\text{ and }\textit{Archaea}} Mn(IV)$$

$$Fe(II) \xrightarrow[\text{Oxidation}]{\textit{Eubacteria}\text{ and }\textit{Archaea}} Fe(III)$$

$$Co(III) \xrightarrow[\text{Reduction}]{\textit{Eubacteria}\text{ and }\textit{Archaea}} Co(II)$$

$$AsO_2^- \xrightarrow[\text{Reduction}]{\textit{Eubacteria}\text{ and }\textit{Archaea}} AsO_2^{4-}$$

$$Se^0 \xrightarrow[\text{Oxidation}]{\textit{Eubacteria}\text{ and }\textit{Archaea}} SeO_3^2$$

$$CrO_4^{2-} \xrightarrow[\text{Reduction}]{\textit{Pseudomonas fluorescens}} Cr(OH)_3$$

Equilibrium and kinetics studies are essential to visualize the mechanism of biosorption. Therefore equilibrium and kinetic models for heavy metals sorption were developed by considering the effect of the contact time, effect of temperature, initial heavy metal ion concentrations, and initial pH. Few commonly used equilibrium and kinetic models for biosorption have been described below.

Equilibrium models

Several empirical models and the mechanistic models (based on mechanism of metal ion biosorption) have been proposed for biosorption to estimate metal uptake capacity of different species. To predict the experimental behavior mechanistic models are recommended (Pagnanelli et al. 2002; Volesky 2003). The Langmuir model (Eq. 1) which is based on monolayer adsorption of solute and the Freundlich model (hetero-geneous surfaces) (Eq. 2) are the two widely utilized equilibrium isotherms.

$$\therefore q_e = \frac{K_L C_e}{1 + K_L C_e} \tag{1}$$

where, q_e is the adsorbent capacity at equilibrium concentration C_e for the formation of monolayer and K_L is the adsorption coefficient.

$$q_e = KC_e^n \tag{2}$$

where, q_e and C_e are the equilibrium metal sorption capacity and equilibrium concentration of adsorbate and K and n are Freundlich co-efficients.

Both the basic models (Eqs. 1 and 2) are not able to explain any mechanisms of sorbate uptake and scarcely have a meaningful physical interpretation for biosorption. The above mentioned two empirical models do not include the external variable, even though they are found suitable in biosorption. Any wastewaters generally contain multiple metal ions so to visualize multi-layer biosorption, other models such as BET model (Eq. 3) and have been developed (Brunauer et al. 1938)

$$q_e = \frac{BQ^o C_e}{(C_s - C_e)[1 + (B-1)C_e/C_s]} \tag{3}$$

where, C_s is the saturation concentration of the adsorbed component, B is a constant which is a measure of the energy of interaction between the solute and the adsorbate surface, and Q^o is the constant indicating the amount of solute adsorbed forming a monolayer.

To visualize multi-metal ions biosorption system, several extended Langmuir models such as Langmuir multi-component model (Eq. 4) has been developed and studied (Langmuir 1918; Volesky 2003; Pagnanelli et al. 2002)

$$q_{ei} = \frac{b_i q_{\max,i} c_{ei}}{1 + \sum_{i=1}^{N} b_i c_{ei}} \tag{4}$$

where, c_{ei} and q_{ei} are the unadsorbed concentration of each component at equilibrium and the adsorbed quantity of each component per g of dried adsorbent at equilibrium, respectively. b_i and $q_{\max,i}$ are derived from corresponding individual Langmuir isotherms.

Kinetic models

For design of biosorption process, kinetics studies (determining rate of the sorption and hydrodynamic parameters) are very important. Kinetic models (based on the capacity of the adsorbent) mostly used to investigate the biosorption phenomenon are the Lagergren's first-order equation (Eq. 5) and pseudo second-order equation (Eq. 6) (Ho 2006).

$$\frac{dq}{dt} = k_1(q_e - q) \tag{5}$$

where, q is the amount of adsorbed pollutant on the biosorbent at time t and k_1 is the rate constant of Lagergren first-order biosorption.

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{6}$$

where k_2 is the rate constant of pseudo second-order biosorption.

Another model used for biosorption is Intra particle diffusion model (Eq. 7). The initial rate of the intra particle diffusion is;

$$q = k_p\left(t^{1/2}\right) + D \quad (7)$$

where k_p is the intraparticle diffusion rate constant and D is a constant that gives idea about the thickness of the boundary layer. In most of the cases the pseudo second-order equation is found more appropriate for biosorption (Ho 2006).

Effective microbial processes for heavy metal transformation

Unlike organic pollutants, heavy metals cannot be destroyed, but must either be converted to a non toxic stable form or removed. Heavy metals are readily biodegradable at one place, but not at another because of different capacities, modes, and rates of biodegradation (Miyata et al. 1998). There are several conventional processes to eliminate heavy metals from contaminated water but that require instrumentation, manpower and technical inputs. A number of methods (adsorption, evaporation, electroplating, ion exchange, membrane filtration, precipitation) have been developed for removal/transformation of toxic metal ions from wastewaters. These conventional technologies are also expensive due to non-regenerable materials used. Microbial based methods using bacteria and fungus are natural, cost effective and safe for heavy metal removal from water bodies (Fig. 1). Some efficient heavy metal transformer bacterial and fungal species in aquatic ecosystem are listed in Table 2. High industrial growth and capricious human activities resulted in the accumulation of heavy metals in the aquatic system. Decontamination of heavy metals from wastewater has been a challenged for a long time. Some reports on microbial transformation of heavy metals came out in successive years via biological methods (Biofiltration, Bioabsorbtion, and Bioremediation). These processes represent a biotechnological advancement as well as a cost efficient tool for the removal of heavy metals from aquatic ecosystem and are discussed below briefly.

Biofiltration

Biofiltration do the capture of heavy metals by microbes and transform it in less or non toxic substance. This process is able to remove high proportion of toxic heavy metals from effluents without production of toxicity (Srivastava and Majumder 2008). This is an important technique and highly recommendable for tropical wastewater where sewage is mixed with industrial effluents. Tripathi and Tripathi (2011) reported the high efficiency of biofiltration by modifying it with ozone to improve the quality of secondary effluent treatment for heavy metal removal. Specific chemical modifications can be done with some oxidizing agents like peroxide, or ozone to increase the biofiltration efficiency for heavy metal removal. Biofiltration is shown to be very effective by Tripathi and Tripathi (2011) in the significant removal of not only heavy metal but also organic and inorganic contents present in the secondary effluent. Microbes do rapid biofiltration of heavy metals as compared to conventional or mechanical processes. Some microorganisms have been identified to possess strong heavy metals removal potential from waste water (Table 2). Bacteria and fungi are accomplished at utilizing the heavy metals rapidly due to their small size and high surface to volume ratio. Bacteria dominate over fungi in biofiltration process because they are smaller and more active than fungi (Scragg 2005). But a few fungi can transform some compound heavy metals which are beyond the metabolic abilities of bacteria (Iram et al. 2015; Sasek et al. 1993). Fungal specie like *Micrococcus* and *Aspergillus* tolerate high concentrations of chromium and nickel from industrial wastewater (Congeevaram et al. 2007). Therefore both are very important for this process. In a few cases microbes may develop a biofilm for rapid biofiltration (Hoppe 1993). Hoppe (1993) have suggested Mn removal on large scale by re-circulating batch cultures of *Leptothrix discophora SP-6*. It would be possible to seed a new manganese biofilter in water. The percentage removal of Mn was very high (>97 %) in many cases and utilized for water treatment effectively. Moreover, chemical modification of adsorbents can also improve the filter efficiency and bacteria and fungi are susceptible to develop their capabilities.

Biosorption

Biosorption is an asset of certain types of dormant microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions. Bacteria and fungi have proven to be a potent heavy metal biosorbents (Table 3). The mechanisms by which metal ions bind to the bacterial and fungal cell surface include covalent bonding, electrostatic interactions, extracellular precipitation, redox interactions, Van der Waals forces or the combination of these processes (Zhang and Li 2011; Mohite and Patil 2014). The negatively charged groups (carboxyl, hydroxyl, and phosphoryl) of the bacterial cell wall adsorb metal cations, which are then retained by mineral nucleation. Biosorption studies of some heavy metals showed that the extent of

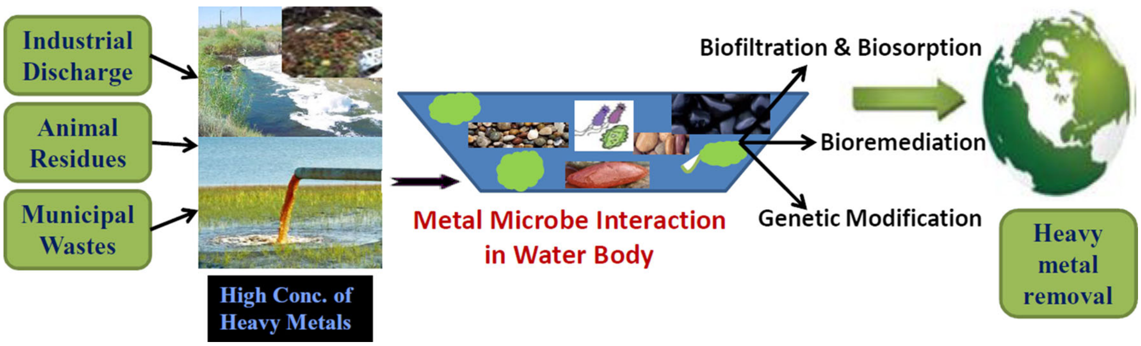

Fig. 1 Microbial processing of toxic heavy metal biotransformation/removal on aquatic ecosystem of the earth

Table 2 Bacteria and fungi used for degradation of heavy metals

Microorganisms	Heavy metals removal	References
Arthrobacter viscosus, E. coli, Klebsiella sp., *Lactobacillus* sp., *Proteus* sp., *Pseudomonas* sp., *Staphylococcus* sp., *Vibrio* sp.	Cd, Fe, Pb, Ni and Zn	Blanquez et al. (2006), Sri-Kumaran et al. (2011), Quintelas et al. (2013), Yan and Viraraghavan (2000)
Bacilli Sp., *Chrollea vulgaria, Enterobacteria, P. fluorescence, Rhizopus archizus, Utrobacter*	As, Cd, Co, Cr, Cu, Ni, and Zn	Thakkar et al. (2006), Rzymski et al. (2014)
Leptrospirillum ferrooxidase, P. aevurginasa, P. thremophillus, P. ferroxidanse	Cd, Cr, Cu, Fe, Ni, Pb and Zn	Miyata et al. (2000), Sand et al. (1992), Osman and Bandyopadhyay (1999)
Aspergillus niger, Coriolus hersutus, Mucor rouxi, Penicillium chrysogenum, Tea fungus, Trametes versicolo	As, Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn	Rzymski et al. (2014), Dursun et al. (2003), Mamisahebei et al. (2007)

Table 3 Heavy metal adsorption capacities of some bacteria and fungi

Heavy metals adsorbed	Microorganism involved	References
Ni^{2+}	*Arthrobacter viscosus*	Quintelas et al. (2013)
Cd^{2+}, Ni^{2+}, Pb^{2+}	*Gluconoacetobacter hansenii*	Mohite and Patil (2014)
$Cr6^{+}$, $U6^{+}$	*Serratia marcescens, S. rubidaea*	Kumar et al. (2011), Zhang and Li (2011)
$Cr6^{+\cdot}$ Ni^{2+}	Mycelial and cocus form of bacteria and fungi	Congeevaram et al. (2007)
Cd^{2+}, Hg^{2+}, Zn^{2+}	*Pseudomonas putida*	Vallas et al. (2000)
Cu^{2+}, Pb^{2+}	*Aspergillus flavus, A. niger*	Iram et al. (2015)
Cu^{2+}	*Candida utilis*	Zu et al. (2006)
Cu^{2+}	*Ganoderma lucidum*	Muraleedharan and Venkobachar (1990)
Cd^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}	*Mucor rouxii*	Yan and Viraraghavan (2000)
Pb^{2+}	*Pleurotus ostreatus*	Osman and Bandyopadhyay (1999)
Ni^{2+}	*Rhodotorula glutinis*	Suazo-Madrid et al. (2011)
Hg^{2+}	*Trametes versicolor and Pleurotus sajur-caj*	Arica et al. (2003)

sorption varies markedly with the metal, chemicals adsorbents/precipitants and the microorganisms (Tyagi et al. 2000). It is also flexible for removal of toxic metals and has easy adaptability for in situ and ex situ application in a range of bioreactor configuration. Quintelas et al. (2013) have shown the bioadsorption of Ni(II) by a bacteria *Arthrobacter viscosus* supported on zeolite in batch and continuous mode at laboratory scale as well as pilot scale. Yan and Viraraghavan (2000) studied the effect of pretreatment of *Mucor rouxii* biomass on bioadsorption of Pb^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+}. Iram et al. (2015) have shown the efficient biosorption and bioaccumulation capability of fungal isolates against Cu and Pb. Different parameters affect the adsorption processes such as contact time, initial metal ions concentration and pH but the role of pH is very significant for the selective adsorption of various heavy metal ions. Basaldella et al. (2007) have used NaA zeolite for Cr(III)removal at neutral pH, while Barakat (2008) used 4A zeolite at high pH for removal of Cr(III). Both group have also reported that Cu(II) and Zn(II) were adsorbed at neutral and alkaline pH respectively, and Cr(VI) was adsorbed at acidic pH while the adsorption of Mn(IV) was achieved at high alkaline pH values. These studies further indicated that the adsorption capacities of the metal ions were found to be strongly dependent on pH. Low cost and higher efficiency even at low metal concentrations make it very attractive in comparison to other physicochemical methods for heavy metal removal. Biosorption strategies for metal removal using microorganisms can reduce the bioavailability and biotoxicity of heavy metals in the environment.

Bioremediation

Bioremediation is the degradation or transformation of pollutants into non-hazardous or less hazardous material. Recently, it is gaining high importance as an alternate technology for removal of heavy metal pollutants from water. Bacteria are generally used for bioremediation, but fungi have also been used for this purpose. Bioremediation by microbes could be an efficient method to reduce the heavy metal load in aquatic environments (Blanquez et al. 2006). Biostimulation or bioaugmentation is applied for the removal of the contaminant from the waste water. The biostimulation is the addition of nutrients, oxygen or other electron donors/acceptors to the coordinated site to increase the population of naturally occurring microorganisms available for remediation, while the bioaugmentation is the addition of microorganisms that may biodegrade the contaminants (Dursun et al. 2003). Bioremediation technology involves the use of microorganisms to reduce or transform contaminants present in soils, water, and air (Alexander 1994). *Alcaligens*, *Bacillus*, *Citrobacteria*, *Escherichia*, *Klebsilla, Pseudomonas*, *Rhodococcus, Staphylococcus* are the microorganisms that are frequently used in bioremediation (Chikere et al. 2012). This process involves biochemical reactions in an organism that result in activity, growth and reproduction of that organism. Chemical processes involved in microbial metabolism consist of contaminants, oxygen, and reactants that convert metabolites to well defined products (Miyata et al. 2000). A key factor for the remediation of heavy metals is that metals are non-biodegradable, but can be transformed through sorption, methylation, and changes in valence state (Arica et al. 2003). Although bioremediation is an attractive solution, quite often the heavy metals are toxic to the microbes actively involved in the bioremediation, making it hard to maintain a high rate of filtration. One possible solution to this problem is genetically engineered microbes, that are resistant to the extreme conditions of the contaminated site and also has bioremediation potential.

Genetically engineered microorganisms for heavy metal removal

The conventional method for the removal of the heavy metals from the polluted site is time consuming, costly, dangerous and may be effective at one site, but not at another because of different derivative capacities, equilibrium, kinetic, and thermodynamic properties. Modification of microbial genomics is a comprehensive approach for the removal of heavy metals and it has been applied on various microorganisms (Sri-Kumaran et al. 2011). Bacterial and fungal genes encoding catabolic enzymes for complex compounds started to be cloned and characterized in early 1980s to prepare a genetically engineered microorganism (GEM).

Once GEMs became a reality, much effort was spent on transformation of heavy metals by bacteria and fungi. GEMs have useful and desired properties for different bioremedial pathway or enzyme with novel biotransformation features. The genetic modification has been done on various bacteria and fungi for the removal of toxic heavy metals from aquatic environment (Table 4). Researchers have successfully produced a multiplasmid containing bacterial strain for transformation of many heavy metals at a time. It is evident that the engineered bacteria and fungi show more removal efficiency versus natural ones (Deng et al. 2003). The engineered bacteria and fungi are more selective with high removal efficiency of heavy metals (Kostal et al. 2004; Valls et al. 2000).

GEMs are useful in reduction of metal toxicity and transform microbes in the natural biodiversity (Scragg 2005). Genes responsible for transformation of heavy metals like As, Cd, Cr, Ni, and Pb have been first identified. Then plasmids have been designed where gene responsible for transformation of these heavy metals were cloned and transformed in bacteria and fungi. Finally potent engineered microbial strains were generated by biotechnologist those are able to degrade a variety of heavy metals and are more selective for heavy metal biotransformation. Modified gene of microorganism occupies high surface volume as compare to older once for biotransformation of toxic heavy metal substances (Rzymski et al. 2014). Sriprang et al. (2003) introduced the phytochelatin synthase gene of *Arabidopsis thaliana* into *Mesorhizobium huakuii* bacteria subsp. *rengei* (strain B3). They have also established the

Table 4 Heavy metals removal efficiency of some genetic modified bacteria and fungi

Bacteria and fungi used for genetic modification	Improvement in the performance of heavy metal removal	Specific modification carried out on the microorganisms	Reference
Escherichia coli	Six folds improved transformation and removal for Ni	Two compatible plasmids, pSUNI and pGPMT3 were used for the expression of a Ni^{2+} transport system in *E. coli*	Deng et al. (2003)
Escherichia coli	Five folds enhanced biotransformation arsenate degradation and removal	The metalloregulatory protein ArsR, was overexpressed in *E. coli* which offers high affinity and selectivity toward arsenite	Kostal et al. (2004)
Mesorhizobium huakuii	Better biotransformation of Cd	Phytochelatin synthase gene was expressed under the control of the *nifH* promoter that increased the ability of cells to bind Cd^{2+}	Sriprang et al. (2003)
Pseudomonas putida	Threefolds enhanced for Cd	Recombinant expression of Metallothioneins protein (strong metal-binding capacity) was expressed	Valls et al. (2000)
Pseudomonas putida	20-folds improved for Cr	Chromium resistance properties encoded by a natural plasmid and transformed in P. *putida*	Mondaca et al. (1998)
Aspergillus fumigatus	Enhanced Fe transformation and removal	Abrogation of extracellular siderophore biosynthesis following inactivation of the acyl transferase SidF or nonribosomal peptide synthetase SidD was done for Fe transformation and removal	Schrettl et al. (2007)
Ganoderma lucidum	Transformation for Cu removal	Modification of *G. lucidum* destroys autolytic enzymes that cause putrification of biomass which finally leads to transformation or adsorption of heavy metals	Muraleedharan and Venkobachar (1990)
Tea fungus	Better adsorption and removal of As and Fe	Chemically pre-treated and modified for adsorption of As and Fe	Mamisahebei et al. (2007)

symbiotic association between *M. huakuii* subsp. *rengei* (strain B3) and an herb *Astragalus sinicus* for better biotransformation of Cd(II). Deng et al. (2003) constructed a genetically engineered *E. coli* (Strain JM109) which simultaneously expresses metallothionein enzyme and a nickel transport system to remove and recover Ni(II) from waste water. Metalloregulatory protein ArsR (offers high affinity and selectivity toward arsenite) was overexpressed in *E. coli* by Kostal et al. (2004) for arsenic removal from water bodies. *Pseudomonas putida* was engineered for over expression of metallothioneins gene to treat heavy metal pollution in industrial sewage (Valls et al. 2000). A 200 kb natural plasmid having chromium resistant property was transferred to *Pseudomonas putida* KT 2441 strain to confer a chromate resistance phenotype and the resistant strain took up 50 % less Cr than the susceptible strain (KT2441) of *P. putida* (Mondaca et al. 1998). *Aspergillus fumigatus* excretes triacetylfusarinine C and fusarinine C to confine extracellular iron found in industrial waste water. Schrettl et al. (2007) used this fungus to capture iron and also show the uses of ferricrocin for fungal hyphal iron storage. Arsenic contamination in ground water poses a severe threat to health. Tea fungus (a symbiont of two yeasts viz., *Pichia* sp. NRRL Y-4810 and *Zygosaccharomyces* sp. NRRL Y-4882 and a bacterium *Acetobacter* sp. NRRL B-2357) was exploited by Mamisahebei et al. (2007) for removal of As(III), As(V) and Fe(II) from ground water samples. The biosorption rate of tea fungus reported against heavy metals (As and Fe) tend to increase with the increase in contact time and adsorbent dosage (Mamisahebei et al. 2007). Muraleedharan and Venkobachar (1990) have enhanced the biosorptive capacity for Cu(II) with the help of engineered mushrooms.

Based on the above discussed research reports, genetically modified bacteria and fungi are the promising recommendations for the transformation or/removal of heavy metals from wastewater. These findings reveal the suitability and distinct use of engineered microbes for heavy metal removal. Depending on the ambient conditions, the GEM mediated biotransformation processing of heavy metal is highly effective and safe. Natural occurring and GEMs are unique for remediation of municipal sewage waste. Use of mixed microbial cultures would be certainly beneficial in multi-contaminated heavy metal solution. The application of genetic engineering in microbes for heavy metal removal has awakened great interest. It is hoped that the above discussed microbial processes for heavy metal transformation would be effective and improve biotransformation efficiency of heavy metals in aquatic ecosystem (Fig. 1).

Conclusion

Living organisms of aquatic ecosystem are directly exposed to toxic heavy metals that are commonly present in ionized form. These heavy metal ions exert adverse effects on aquatic life. Bacteria and fungi can significantly decrease the toxic heavy metal concentration and distribution in water bodies by biotransformation. From the above discussion it is concluded that there is a high possibility of large scale application of biofilter and biosorption in heavy metal biotransformation. It may be utilized by the microbial population as a growth substrate for the removal of toxic heavy metals from polluted water (Rzymski et al. 2014). More information is needed about microbes mediated transformation of heavy metals to make eco-friendly environment. Heavy metals seem to be more toxic for aquatic ecosystem and their high range in the environment has proven hazardous (Sharma and Kuhad 2010). More efforts should be made to prevent toxic sewage waste discharge into water.

Microbial activities are very important for removal of toxic heavy metals. The metal removal capacity of bacteria and fungi is far better, more beneficial and eco friendly than other conventional methods and various studies suggest that microbial process are most promising for biotransformation of toxic heavy metals in aquatic ecosystems. Biosorption has a good potential of heavy metal biotransformation. For example, Quintelas et al. (2013) have reported high adsorption capacities of Ni(II) by *Arthrobacter viscosus* supported on zeolite 13 X. High sorption capacity (44.45 mg/g at 25 °C and 63.53 mg/g at 70 °C) by acetone pretreated *Rhodotorula glutinis* biomass was shown by Suazo-Madrid et al. (2011). The adsorption capacity of nickel(II) on *Parthenium hysterophorous* ash was also high and percent removal of Ni increased from 67.30 to 97.54 % (Singh et al. 2009). Many researchers have also shown the adsorption capacity of other microbes using different adsorbents for different heavy metals (Yan and Viraraghavan 2000; Basaldella et al. 2007; Barakat 2008).

Heavy metal biotransformation done by natural and genetically modified bacteria and fungi is also very effective and provides a promising and spontaneous approach for the removal of a wide variety of ecotoxic heavy metals. The accomplishments in microbial cloning techniques improve the heavy metal removal efficiency including the reduction in the treatment cost of contaminated water. Genetically modified microbes are capable of removing heavy metals up to ppb level and are also cheaper for the treatment of industrial wastewater. GEMs have improved heavy metal biotransformation ability, and their application could be used for bioremediation of heavy metals from aquatic environments. Optimization and operational conditions could limit the practical and fast application of microbes in biotransformation because a huge number of heavy metals having toxicological effects on environment could be targeted. Current understanding on this particular topic is not sufficient and there is a gap between existing knowledge and its application. More research in this area is needed to reduce environmental heavy metal toxicity and enjoy a more sustainable future.

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