



Review

## Biological approaches to tackle heavy metal pollution: A survey of literature



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### ABSTRACT

Pollution by heavy metals has been identified as a global threat since the inception of industrial revolution. Heavy metal contamination induces serious health and environmental hazards due to its toxic nature. Remediation of heavy metals by conventional methods is uneconomical and generates a large quantity of secondary wastes. On the other hand, biological agents such as plants, microorganisms etc. offer easy and eco-friendly ways for metal removal; hence, considered as efficient and alternative tools for metal removal. Bioremediation involves adsorption, reduction or removal of contaminants from the environment through biological resources (both microorganisms and plants). The heavy metal remediation properties of microorganisms stem from their self defense mechanisms such as enzyme secretion, cellular morphological changes etc. These defence mechanisms comprise the active involvement of microbial enzymes such as oxidoreductases, oxygenases etc, which influence the rates of bioremediation. Further, immobilization techniques are improving the practice at industrial scales. This article summarizes the various strategies inherent in the biological sorption and remediation of heavy metals.

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## 1. Introduction

Recent years have evinced an unparalleled population growth and an accelerated pace of industrialization in line with it. Although, the quality of human life has substantially improved over the years, it is inevitable not to ignore that these developmental activities have taken place at the cost of the quality of our environment. During the last century, mining, electroplating, smelting, fertilizer, pesticides, tanneries, paper and electronic industries have accounted for the release of large amounts of heavy metals and petroleum hydrocarbons into the natural ecosystem, which has been reported to have disrupted the physiological functions in biological systems (Taiwo et al., 2016; Arivalagan et al., 2014). Environmental contamination can also occur through leaching of heavy metals, metal corrosion, atmospheric deposition, sediment resuspension to soil and ground water and metal evaporation from the water resources (Weerasundara et al., 2017; Francová et al., 2017). Hence, sediments constitute the major phase of contamination by metals in the aquatic systems (Nagajyoti et al., 2010). Among the pollutants, the hazardous heavy metals such as Arsenic (As), Cadmium (Cd), Lead (Pb), Copper (Cu), Chromium (Cr), Nickel (Ni), Zinc (Zn), Aluminum (Al) and Manganese (Mn) have known to be the major threats to the environment (Ullah et al., 2015; Dhanarani et al., 2016; Karthik et al., 2017a). These heavy metals impart serious health issues both to humans and ecosystems (Zeraatkar et al., 2016; Chen et al., 2015; Ullah et al., 2015). Source of various heavy metals are listed in Table 1.

The heavy metal pollutants can enter into the environment through natural and anthropogenic ways and can be deposited in

soils, water bodies or in the air (Kuppusamy et al., 2017; Chen et al., 2015). Humus, the organic material present in the soil (which also makes the soil look green) has a high affinity for the heavy metal cations and extracts them from the water that passes through the soil. Roots of crops and other plants pick up these elements along with water and pass on to plants and then plants to animals. Heavy metals are also retained in the soil by adsorption on mineral particles present in the soil and precipitation reactions (Manafi et al., 2012). In water, particles with the adsorbed heavy metals settle to the bottom and the sediments may accumulate over them (Kang and So, 2016). If organisms consume these particles, the heavy metals enter the food web, thereby magnifying the after effect. While in the food chain, the heavy metals, which are generally non-biodegradable, get accumulated to result in multiple health hazards such as damage of lung, kidney, liver, pancreas and nervous disorders (Arivalagan et al., 2014; Kumar et al., 2017). For instance, accumulation of Cr(VI) and its reduced counterpart Cr(III) in the cells has been known to result in DNA damage. Similar adverse health effects have been reported for other heavy metals and hence, U.S. Environmental Protection Agency (EPA) and World Health Organization (WHO) have set a maximum permissible limit for every heavy metal in various systems (Kumar et al., 2017).

Earlier, methods such as chemical precipitation, coagulation, flocculation, filtration, reverse osmosis, ion exchange, membrane process, biosorption, aerobic and anaerobic microbial degradation (Kuppusamy et al., 2017; Carolin et al., 2017), have been extensively explored for their effectiveness in the removal of metals from different environmental media. Among these mechanisms, biosorption is considered as an innovative technology and remedial

**Table 1**  
Sources of heavy metal contamination.

S.No	Sources	Heavy metals	Severity	References
1	Industrial waste: Mining, pharmaceutical, textile, petrochemical and oil spills and E-waste	Zn, Ni, Cu, Cr, Pb, Cd, Mn	High	Schaider et al., 2014; Mwinyihija, 2010
2	Air-borne sources: Stack, vehicular and fugitive emissions.	As, Cd, Pb	Wide area distribution- Severe	Wuana and Okieimen, 2011
3	Fertilizers	Co, Cu, Fe, Mn, Mo, Ni, Zn	Average	Roberts, 2014
4	Pesticides	Cu, Hg, Mn, Pb, and Zn	Low	Tchounwou et al., 2012
5	Sewage Sludge	As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn, Tl and Sb	Low to average	Shamuyarira and Gumbo, 2014

strategy in view of its cost effectiveness and eco-friendly nature (Arivalagan et al., 2014; Congeetaram et al., 2007). Noteworthy findings by Zeraatkar et al. (2016), who have reported that the algal biomass subjected to lipid and biofuel production, could still be used as a potential biosorbent. The potential of waste biomaterials as superior biosorbents for wastewater remediation has been put forth by other researchers as well (Favara and Gamlin, 2017).

Generally, bioremediation involves the adsorption of the soil contaminants on organic matter or reduction of the metal bioavailability by microorganisms (Kuppusamy et al., 2017; Mukherjee et al., 2017; Boopathy, 2000). However, most of the researchers suggest the preferential use of microorganisms over organic matter to remove/reduce the heavy metal concentration from the contaminated sites. Such an inherent property of microbial communities has been effectively utilized to reduce, degrade or immobilize hazardous contaminants and clean up the polluted environments. The following sections elucidate the various mechanistic aspects of bioremediation processes in detail.

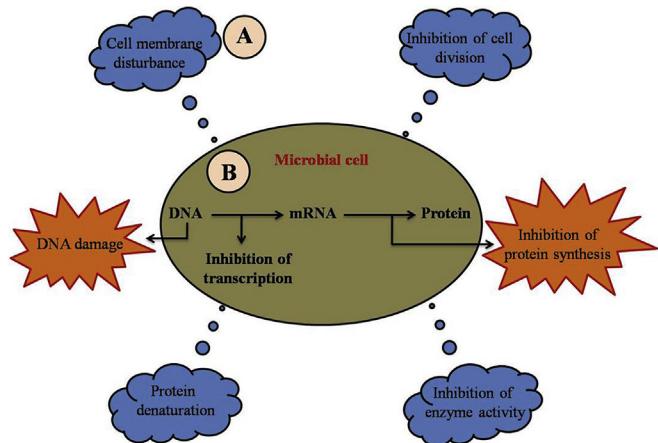
## 2. Microorganisms- the key players in bioremediation

In general, bioremediation processes are categorized as bioaccumulation, biosorption, biotransformation and biominerilization using microorganisms, whereas phytoremediation techniques are carried out using plants and plant parts in a metal containing environment. Among these, biosorption is a promising technology, which plays a central role in the removal of heavy metals. Biosorption is an emerging technology and a passive uptake process, which is mostly reversible and metabolism-independent involving adsorption on the cell surfaces of biological materials (Arivalagan et al., 2014). Bioaccumulation is a complex process that involves the accumulation of heavy metals inside the cellular components. The major advantage of microbial biosorption is its low operational cost, simple, high effective and environmental friendly methodology (Karthik et al., 2017a; Congeetaram et al., 2007).

Heavy metals such as Cu, Zn, Ni, Cr, Co, Mo, Fe, and Mn are essential micronutrient for various organisms including microorganisms, plants and animals. However, when metal concentrations exceeded their threshold level, metals induced various physiological, biochemical and genotoxic effect on all type of living forms (Jaishankar et al., 2014; Emamverdian et al., 2015). Heavy metal concentrations highly influence the microbial communities in two different ways; (i) inhibition of metabolic function and (ii) modulation in genetic materials. Heavy metals have the ability to inhibit the various physiological processes such as cell membrane distribution (Karthik et al., 2016; Khan et al., 2009; Yuan et al., 2015), inhibition of cell division (Banfalvi, 2011) and enzyme activity (Wyszkowska et al., 2013; Khan et al., 2009) and denaturation of protein (Banfalvi, 2011). Moreover, heavy metals can damage the genetic materials (Sobol and Schiestl, 2012; Banfalvi, 2011) and inhibit the transcription process (Gundacker et al., 2010). Fig. 1 clearly highlights the toxicity effect of heavy metals on microorganisms.

### 2.1. Bioremediation by bacteria

The use of living and non-living bacteria as biosorbents has been extensively studied by several researchers. Microbial biomass is a potential alternative for the uptake of heavy metals from different polluted media. The inherent advantages of microbe mediated bioremediation are that the microbial biomass (eg. *Citrobacter*, *Pseudomonas*, *Streptomyces*, *Bacillus* etc.) can be acquired as a left-over product akin to fermentation industries and the microbes may take up a substantial amount of heavy metal ions, resulting in the transfer of metals to a contaminated matrix of biomass (Dhanarani



**Fig. 1.** Toxicity effects of heavy metals on microorganisms. Toxicity of heavy metals on microorganisms occur in two phases (A) inhibition of metabolic functions and (B) modulation in genetic materials.

et al., 2016; Arivalagan et al., 2014). Among the microbes, bacteria have specific genetic mechanisms and play an important role in the mitigation of environmental contamination. Some important bacterial strains such as *Bacillus* and *Pseudomonas* sp. have been widely used for the removal of heavy metals from wastewater and soil because of their high metal binding affinities (Ullah et al., 2015; Arivalagan et al., 2014; Bachate et al., 2013; Li and Ramakrishna, 2011). Bacterial functional groups such as hydroxyl, carboxyl, sulfonate, amide and phosphonate groups are mainly involved in the metal uptake process from aqueous solutions (Arivalagan et al., 2014; Huang and Liu, 2013). Uptake of metal ions by different bacterial species is given in Table 2.

Various studies have highlighted that the heavy metal bioremediation props up from the basic self defense mechanism of bacteria that dictates cell surface changes and agglomeration of cells to mitigate the toxic effects of heavy metals. The aforementioned observations have been proved with the help of high resolution microscopic images. In Cr(VI) free control samples, the cells appeared to be elongated with a clear smooth surface and are discrete. On the other hand, Cr(VI) treated cells appeared with irregular cell surfaces and the cells were arranged together forming clump/adherence (Fig. 2).

The microbial cell wall is mainly responsible for metal binding (Siddiquee et al., 2015). Anionic nature of microbial surfaces enables them to bind metal cations through electrostatic forces. Gram-positive bacteria contain a thicker cell wall, which is composed of peptidoglycan, teichoic and teichuronic acids. In Gram-negative bacteria, teichoic, teichuronic acids are absent and peptidoglycan layer is thin. Compared to Gram-negative bacteria, Gram-positive bacteria are more efficient in trapping metal ions. The prominent role of the bacterial cell surface components in biosorption has been highlighted by the findings of Karthik et al. (2017a). In a comprehensive study on Cr(IV) biosorption by a novel haloalkaliphilic bacterium, it was observed that both the intracellular and extracellular reducing machineries and the cell surface functional groups such as alkanes, amide and amines are involved in chromium biosorption and immobilization on cell surfaces. Fig. 3 summarizes the Cr(VI) reduction mechanism by bacterial species.

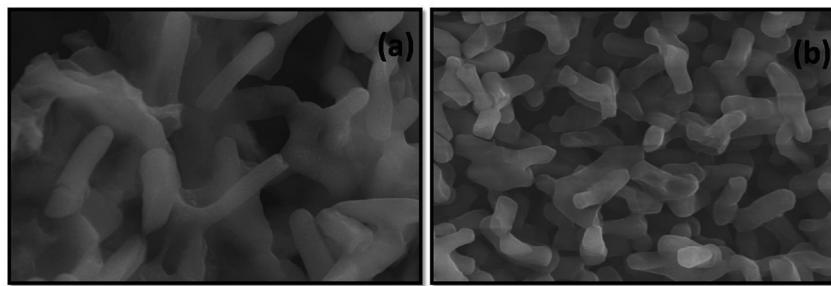
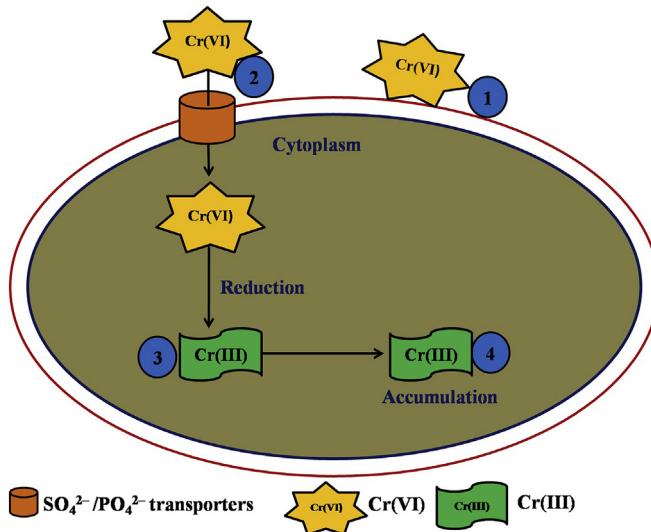
### 2.2. Bioremediation by fungi

Filamentous fungi are ubiquitous microorganisms and can be

**Table 2**

Adsorption potential of different bacterial cultures for the removal of metal ions.

Biosorbent	Metals	Adsorption capacity (mg/g)	References
<i>Bacillus licheniformis</i>	Cr(VI)	62	Zouboulis et al., 2004
<i>Bacillus firmus</i>	Pb, Cu, Zn	467, 381, 418	Salehzadeh and Shojaosadati, 2003
<i>Bacillus coagulans, Bacillus megaterium</i>	Cr(VI)	39.9	Srinath et al., 2002
<i>Enterobacter sp. JI</i>	Cd	46.2	Lu et al., 2005
<i>Bacillus licheniformis</i>	Cd	142.7	Zouboulis et al., 2004
<i>Bacillus licheniformis, Escherichia coli, Pseudomonas fluorescens, Salmonella typhi</i>	Cd, Pb, Zn	—	Basha and Rajaganesh, 2014
<i>Bacillus cereus</i>	Hg	104.1	Sinha et al., 2012
<i>Desulfovibrio desulfuricans</i>	Cu, Ni, Cr	98.2, 90.1, 99.8	Kim et al., 2015
<i>Enterobacter cloacae</i>	Pb	2.3	Kang et al., 2015
<i>Kocuria rhizophila</i>	Cd, Cr	9.07, 14.4	Haq et al., 2016
<i>Micrococcus luteus</i>	Cu, Pb	408, 1965	Puyen et al., 2012
<i>Lactobacillus sp.</i>	Cu	0.046	Schut et al., 2011
<i>Pantoea agglomerans</i>	Cr	—	Sikander et al., 2012
<i>Alcaligenes sp.</i>	Pb	56.8	Jin et al., 2017
<i>Ochrobactrum intermedium, Cupriavidus metallidurans</i>	Cu, Cr	—	Fan et al., 2014

**Fig. 2.** SEM images of *Bacillus cereus* (a) Cr(VI) untreated biomass (b) Cr(VI) treated biomass.**Fig. 3.** Conceptual diagram of Cr(VI) reduction mechanism by bacteria. The intracellular reduction involving four simultaneous processes (1) Cr(VI) interaction and bio-sorption, (2) Cr(VI) transport, (3) Cr(VI) reduction and (4) Cr(III) accumulation.

observed in all ecological niches since they have the ability to adapt the metabolism to varying carbon and nitrogen sources (Saratale et al., 2007). Fungi are well known to tolerate and detoxify heavy metal contaminated effluents. Fungal cell wall consists of chitin and other polysaccharides along with proteins, lipids, polyphosphates as well as inorganic ions cementing the cell wall. Owing to greater cell-to-surface ratio, fungi have a greater tendency to come in physical and enzymatic contact with the surroundings. Fungal

biomass seems to be a good sorption material as it can be easily cultured in large scales using simple fermentation techniques (Congeevaram et al., 2007). Table 3 enumerates the fungal species commonly used as biosorbents. Fungal biomass is inexpensive and is readily available as the waste product of various enzyme based industries. The mechanism involved in fungal detoxification of heavy metal contaminated environment includes valence transformation, intra and extracellular precipitations as well as active uptake (Thatoi et al., 2014). Typically, the high content of carboxyl groups in the mannuronic and guluronic acids of the cell wall polysaccharides and the protosufficiency enhance heavy metal biosorption (Raja et al., 2015).

Jacob et al. (2017) have reported that the cell wall morphology is chiefly altered due to heavy metal stress. Fig. 4 shows the SEM images of Pb treated and untreated (control) fungal cells. It is evident from the figure that the Pb stress in the external media would have induced an increase in the cytosolic pressure in the fungal cells due to the surge in the stress response within the cells. Similar results have been reported for fungal species like *Pleurotus ostreatus*, *Trametes versicolor*, *Bjerkandera adusta*, *Lentinula edodes*, *Irpea lacteus*, *Agaricus bisporus*, *Pleurotus tuberregium* and *Pleurotus pulmonarius* etc., which indicate the active role of fungi as superior biosorbents (Rhodes, 2014).

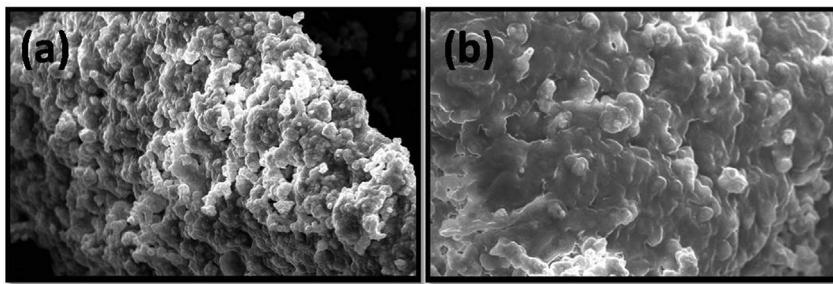
### 2.3. Algae mediated bioremediation

Algae are photosynthetic organisms having the ability to transform solar power into biochemical energy and having faster growth rates relative to forest-derived biomass, agricultural residues and aquatic species. On the basis of size, they are classified into microalgae, which are microscopic, unicellular photosynthetic plants, and macroalgae, which are multicellular occurring near the

**Table 3**

Adsorption potential of different types of fungal biomass as biosorbents for the removal of metal ions.

Fungal strains	Elements	Uptake capacity (mg/g)	References
<i>Ganoderma lucidum</i>	Cr, Cu, Pb	—	Muter et al., 2002
<i>Pleurotus sapidus</i>	Cd, Hg	127, 287	Yalcinkaya et al., 2002
<i>Mucar rouxi</i>	Ni	0.36	Magyarosy et al., 2002
<i>Aspergillus niger</i>	Pb	5.3–34.4	Dursun et al., 2003
<i>Mucar rouxi</i>		4.06	Yan and Viraraghavan, 2001
<i>Aspergillus niger</i>	Cr	5.1–6.6	Dursun et al., 2003
<i>Saccharomyces cerevisiae</i>	Mn	22.5	Fadel et al., 2017
<i>Lepiota hystrix</i>	Pb, Cu	3.89, 8.50	Kariuki et al., 2017
<i>Pleurotus platypus</i>	Ag	46.7	Das et al., 2010
<i>Rhizopus oryzae</i>	Cu	34	Fu et al., 2012
<i>Aspergillus brasiliensis, Penicillium cirtinum</i>	Cu, Mn, Zn	—	Pereira et al., 2014
<i>Aspergillus niger,</i>	Pb, Ni, Cr	—	Dwivedi et al., 2012
<i>Aspergillus flavus</i>		—	
<i>Aspergillus terreus, Trichoderma longibrachiatum</i>	Pb, Cd, Cr	—	Joshi et al., 2011
<i>Penicillium citrinum</i>	Cu	—	Verma et al., 2013
<i>Aspergillus niger</i>	Cr	11.792	Mondal et al., 2017

**Fig. 4.** SEM images of *Aspergillus terreus* (a) Pb untreated biomass (b) Pb treated biomass.

seabed (Saratale et al., 2017a; Vijayaraghavan and Balasubramanian, 2015). An alga thrives in all kinds of aquatic habitats viz. freshwater and marine as well as in moist soil. Algae have not been very well documented as a biosorbent compared to fungi and bacteria. Bioaccumulation by algae is supported by various metabolic processes (Zeraatkar et al., 2016). Biosorption is a surface phenomenon and usually involves sequestration on the cell surface. Therefore, modification of algal cell wall may greatly alter the binding of metal ions. Various methods have been employed for the modification of cell wall in algae in order to enhance the metal binding capacity of biomass and to elucidate the inherent mechanism. Marine algae possess large quantities of biopolymers that may bind with heavy metals. Large quantity of heavy metals may be accumulated by various algal species are dependent and independent of their metabolism. Brown and red algae are the most promising seaweeds for biosorption (Flores-Chaparro et al., 2017; Ajabi and Chouba, 2009). Special polysaccharides of algal cell walls have potential metal ion binding sites. Polysaccharides in the cell walls of algae can provide amino and carboxyl groups as nitrogen and oxygen moieties that could form co-ordinate bonds with metal ions. Proteins can constitute 10–70% of cell wall composition in green algae whereas 37–50% in red algae. Number of binding sites depends upon the chemical composition of the cell wall. Alginic acid in brown algae contributes to 40% of its dry weight. Metal ions can also be electrostatically bonded to non-protonated carboxyl, oxygen and sulphate. Various studies related to the application of algae as a biosorbent are summarized in Table 4.

Researchers such as Tran et al. used the gelatin colonies of cyanobacteria isolated from the rice fields in Phu Tho Province, Viet Nam (Al-VN) for the removal of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from water. Both biosorption and desorption processes were investigated in their study. 0.1 M EDTA 2Na and 0.1 M  $\text{HNO}_3$  acted as good

desorbents for the recovery of biomass making the adsorbent to be reusable (Tran et al., 2016). The use of algae was found to be double beneficial viz. for wastewater treatment and biofuel production. In a recent study, Zeraatkar et al. (2016) reviewed that the algal biomass which had been utilized for the production of lipid and biofuel could be utilized effectively to neutralize heavy metal ions in wastewater. According to the authors, the algal cellular structure would be largely dependent on the operating conditions such as initial concentration, pH and reaction time etc. Furthermore, genetic modifications of the algal strains, proper pretreatment and immobilization could enhance the potential of algae as biosorbents (Favara and Gamlin, 2017).

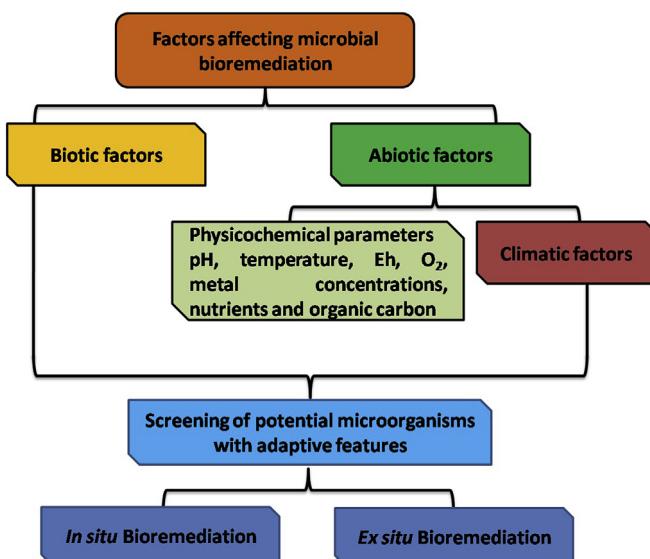
### 3. Factors affecting heavy metal bioremediation

Bioremediation is a complex biological process of the microorganisms. Microbes are able to reduce the bioavailability of heavy metals by the production of organic and inorganic acids (eg., citric and sulfuric acid), reduction, oxidation and production of complexing agents (eg., cyanide) (Gadd, 2010). In this scenario, various biotic and abiotic factors highly influence the growth and metabolic functions of the microorganisms, thereby reducing their bioremediation efficiencies (Govarthanan et al., 2016). In general, microorganisms have their innate tolerant ability to get adapted to the harsh environmental conditions; however, they have certain limitations. Therefore, it is necessary to understand the various factors limiting the microbial reduction in order to adopt a suitable strategy to optimize the process of heavy metal bioremediation (Karthik et al., 2017c; Srivastava et al., 2014). Factors affecting the bioremediation efficiency of the microorganisms could be grouped into; (i) biotic and (ii) abiotic factors (physicochemical parameters and climatic conditions). Fig. 5 highlights the environmental challenges

**Table 4**

Adsorption potential of different algae as biosorbents for the removal of metal ions.

Algal strains	Metal	Uptake capacity (mg/g)	References
<i>Spirogyra</i> sp.	Cr	133.30	Gupta et al., 2006
<i>Aphananthece halophytica</i>	Zn	133	Incharoensakdi and Kitjharn, 2002
<i>Spirogyra</i> sp.	Zn	—	Bishnoi et al., 2007
<i>Chlorella sorokiniana</i>	Cd	13.33	Akhtar et al., 2003
<i>Dunaliella</i> sp.	Cr	58.3	Dönmez and Aksu, 2002
<i>Sargassum wightii</i>	Ni	37.2	Vijayaraghavan et al., 2005
<i>Sargassum</i> sp.	Ni	181	Kalyani et al., 2004
<i>Palmaria palmata</i>	Pb	15.17	Prasher et al., 2004
<i>Spirulina maxima</i>	Pb	—	Gong et al., 2005
<i>Spirogyra hyalina</i>	Cd, Hg, Pb, As	—	Kumar and Oommen, 2012
<i>Micrasterias denticulata</i>	Cd	—	Volland et al., 2013
<i>Cystoseira barbata</i>	Cd, Ni, Pb	37.6, 78.7, 196.7	Yalçın et al., 2012
<i>S. neglecta</i>	Cu	30.17	Singh et al., 2012
<i>Cladophora</i> sp.	Pb	45.4	Lee and Chang, 2011
<i>Cladophora hutchinsiae</i>	Se	74.9	Tuzen and Sarı, 2010
<i>Chlorella vulgaris</i>	U	14.3	Vogel et al., 2010
<i>Scenedesmus obliquus</i>	Zn	429.6	Monteiro et al., 2011
<i>Chara aculeolata</i>	Pb, Cd, Zn	105.3, 23.0, 15.2	Sookswat et al., 2016
<i>Nitella opaca</i>	Pb, Cd, Zn	104.2, 20.5, 13.4	Sookswat et al., 2016
<i>Eucheuma denticulatum</i>	Pd, Cu, Fe, Zn	81.97, 66.23, 51.02, 43.48	Rahman and Sathasivam, 2016
<i>Ulva lactuca</i>	Cu <sup>2+</sup> , Cd <sup>2+</sup> , Cr <sup>3+</sup> , Pb <sup>2+</sup>	64.5, 62.5, 60.9, 68.9	Ibrahim et al., 2016

**Fig. 5.** Environmental challenges faced by microorganisms during bioremediation.

faced by microorganisms during bioremediation process.

### 3.1. Biotic factors

Biotic factors greatly influence the bioremediation efficiency of the microorganisms by changing cell size and composition, extra-cellular product formation, etc. The biomass concentration is one of the important biological factors for microbial bioremediation (Gokhale et al., 2008; Finocchio et al., 2010). Park and Choi (2002) suggested that at low biomass concentrations, metal removal efficiency of the microorganisms was higher when intercellular space was more. When biomass concentration is in its equilibrium level, heavy metals in the reduction medium not only get adsorbed to the biomass surface but also enter into the intracellular part facilitated by the concentration gradient of the metal (Vasudevan et al., 2002). On the other hand, higher concentration of biomass restricts the interaction of heavy metals to the binding sites of microbial surfaces (Abbas et al., 2014). Electrostatic interactions between cells

play important roles in heavy metal remediation by microorganisms; high biomass induces the shell effect on the outer structure of the microorganisms (Romera et al., 2007). Higher biomass concentration is known to cause cell aggregation, which subsequently reduces the intercellular distance resulting in decreased metal removal (Fadel et al., 2017). Terry and Stone (2002) reported that the higher biomass concentration of *Scenedesmus abundans* reduced the bioremediation of Cu(II) and Cd(II). Romera et al. (2007) also investigated the bioremoval efficiency of different algal strains for different metal ions and documented that the maximum removal was observed at the lowest biomass concentrations. Similar results have been documented for *Microcystis* (Pradhan and Rai, 2000), *Bacillus subtilis* and *Pseudomonas aeruginosa* (Tarangini and Satpathy, 2009) and *Saccharomyces cerevisiae* (Fadel et al., 2017).

### 3.2. Abiotic factors

Similar to biotic factors, abiotic factors also affect heavy metal bioremediation efficiency of microorganisms. The various abiotic factors explained in this review are the physicochemical parameters (temperature, pH, metal ion concentration, O<sub>2</sub>, redox potential (Eh), nutrient and organic carbon) and climatic conditions.

#### 3.2.1. Physicochemical parameters

**3.2.1.1. Effects of temperature.** Temperature of the reduction medium greatly influences the bioremediation of heavy metals, firstly, by its direct effect on physicochemical state of the contaminants and secondly, through its effect on the metabolic activity of microorganisms. The metabolic activity of microorganisms increases along with the temperature upto optimum, while further increment in temperature may reduce the metabolic activity of organisms by enzyme denaturation and the organisms may either become less active or die (Thomson et al., 2017). Moreover, temperature higher than the optimum may induce modifications in ribosomal conformations thereby reducing protein synthesis (de Groot and Ventura, 2006). On the other hand, temperatures lower than the standard optima negatively affect the membrane fluidity and prevent the functioning of transport systems. These changes would affect the mobility of substrates into the cells, thereby affecting the growth rates (Barria et al., 2013). Extreme temperature (either low or high) kills the microorganisms and affects gas

solubility.

In general, the optimum temperature for *in situ* bioremediation process is around 20 to 40 °C (mesophilic). Previously, several researchers have observed that the optimum heavy metal remediation occurred in mesophilic conditions. Majority of the microorganisms such as *Acinetobacter* sp. (Panda and Sarkar, 2012), *Aspergillus niger* (Gu et al., 2015), *Bacillus cereus* (Naik et al., 2012), *Botrytis cinerea* (Akar et al., 2005), *Enterobacter aerogenes* and *Rhizopus oryzae* (Fu et al., 2012), *Ochrobactrum* sp. (He et al., 2009), *Paenibacillus* sp. (Govarthanan et al., 2016), *Rhizobium* sp. (Karthik et al., 2016) and *Vigribacillus* sp. (Mishra et al., 2012) showed the maximum heavy metal remediation under mesophilic conditions. This might have been due to the maximum activities of the microbial enzymes at optimal mesophilic conditions. Aksu (2001) studied the influence of different temperatures on Cd(II) and Ni(II) bioremediation by *Chlorella vulgaris*. The maximum bio-remediations of Cd(II) and Ni(II) were observed at 20 and 45 °C, respectively. However, some thermophilic microorganisms exhibit maximum growth rates and metal remediation abilities above 45 °C (moderately thermophilic) to 80 °C (hyperthermophiles). These microorganisms could hence prove beneficial in the remediation cascade using compost heaps or biopiles since the temperature of the soil/sediment in such systems may reach 70 °C or higher during initial active phase (Sar et al., 2013). Ghalib et al. (2014) reported that the thermophilic *Bacillus cereus* strains TA2 and TA4 effectively reduced Cr(VI) at 55 °C. Similarly, Özdemir et al. (2013) also reported the maximum removal of Cd(II), Cu(II), Co(II) and Mn(II) by *Geobacillus thermantarcticus* and *Anoxybacillus amylolyticus* at 60 °C. Apart from these, Zeraatkar et al. (2016) suggested that the variations in temperature cause the major differences in growth and metal biosorption abilities of various microorganisms.

**3.2.1.2. Effects of pH.** pH is another important factor in heavy metal bioremediation since it has the ability to modulate the microbial growth, enzyme activity, metal complexation chemistry and behavior of the cell surface functional groups of microorganisms (Gupta and Rastogi, 2008). Majority of the heavy metal bioconversion processes occur enzymatically; the unfavorable medium pH may affect the enzyme ionization, which in turns affects the metal remediation efficiency of the organisms. Several microorganisms such as *Acinetobacter junii* and *Escherichia coli* (Samuel et al., 2012), *Bacillus* sp. (Naik et al., 2012), *Cellulosimicrobium funkei* (Karthik et al., 2017a), *Micrococcus luteus* (Puyen et al., 2012), *Lentinula edodes* (Wang et al., 2017), *Pannobacter phragmitetus* (Xu et al., 2011), *Pleurotus platypus* (Das et al., 2010), *Pseudochrobactrum saccharolyticum* (Long et al., 2013), *Pseudomonas aeruginosa* (Oves et al., 2013), *Trichoderma* sp. (Mohsenzadeh and Shahrokh, 2014) and *Vigribacillus* sp. (Mishra et al., 2012) have efficiently reduced heavy metal bioavailability at neutral environmental conditions. At optimal pH, the enzymatic activities as well as heavy metal remediation efficiencies of the microorganisms increased significantly.

Alteration in the pH of reduction medium can significantly reduce the metal bioavailability and solubility. For instance, the solubility of cadmium was reduced while increasing the pH from 6 to 7 in 1.3 mM phosphate (Olaniran et al., 2013). At acidic conditions, cell surface functional groups may change their properties and may not interact significantly with metal ions. Similarly, Arivalagan et al. (2014) also reported that the interaction of hydronium ions with the cell surface functional groups of microorganisms would reduce the intensity of negative charge, which could result in reduced metal adsorption as well as reduction at acidic conditions. Similarly, alkaline pH had also affected the remediation efficiency of microorganisms. Under alkaline conditions, metal ions form hydroxo-metal complexes by replacing protons. Moreover, alkaline environment increases the logarithmic

phase of microorganisms, which significantly reduces the removal rate of microorganisms (Govarthanan et al., 2016). Interestingly, some microorganisms can efficiently reduce metals at alkaline conditions. For instance, *Ochrobactrum* bacterial strain CSCr-3 efficiently reduced Cr(VI) at pH 10 (He et al., 2009). Similarly, alkaliphilic metal reducing *Halomonas* genus remediates heavy metal at pH 10.5 (Watts et al., 2015). These microorganisms offer an efficient strategy for heavy metal remediation under extreme pH conditions (Long et al., 2013). Redox potential and pH of the environment also determines the speciation and mobility of the heavy metals. Redox reaction affects the process related to metal binding (sorption and desorption), precipitation, complex formation and speciation of the heavy metals (Popenda, 2014). Because of these facts, redox potential is also considered as a major influencing factor for microbial bioremediation of heavy metals.

**3.2.1.3. Effects of metal ion concentration.** Heavy metals usually have the ability to reduce various cellular functions of microorganisms and their effects are concentration dependent. Heavy metal removal efficiency of the microorganisms increases as the initial metal concentrations increases (Karthik et al., 2016). Moreover, heavy metal concentration at lower levels are positively involved in various physiochemical behaviors of microorganisms. However, at elevated levels, heavy metals seriously affect the growth and metabolic activities of microorganisms (Singh et al., 2010). Metal removal efficiency varied based on microorganisms and heavy metal concentrations. For instance, *Micrococcus luteus* efficiently removed 408 mg/g of Cu after 12 h treatment (Puyen et al., 2012). However, *Desulfovibrio desulfuricans* removed 98.2 mg/g of Cu after 168 h treatment (Kim et al., 2015). Similarly, Dursun et al. (2003) reported that *A. niger* strain removed 15.6 mg/g of Cu after 1 h incubation. These variations might have been due to the genetic makeup of microorganisms as well as the composition of the reduction medium (Hobman and Crossman, 2015).

Previously, several researchers documented the toxic nature of higher metal concentrations on bioremediation efficiency of microorganisms. Congeevaram et al. (2007) reported that the increasing concentrations of Cr(VI) and Ni(II) inhibited the growth and metabolic functions of *Aspergillus* and *Micrococcus* sp. Higher concentrations of Cu, Cd and Pb reduced the growth and metal removal by *Aspergillus*, *Penicillium* and *Cephalosporium* sp. (Hemambika et al., 2011). Similarly, *Cellulosimicrobium funkei* strain AR8 reduced 100, 150 and 200 µg/ml of Cr(VI), completely. However, while increasing the Cr(VI) concentration to 250 µg/ml, Cr(VI) reducing efficiency of the bacterial strain got reduced significantly (Karthik et al., 2017b). Similarly, *Chlorella vulgaris* biomass was able to remove 69% and 80% of 2.5 ppm of Ni (II) and Cu (II) ions, respectively. In other words, while increasing the Ni(II) and Cu(II) concentration to 10 ppm, removal efficiency was reduced to 37 and 42%, respectively (Mehta and Gaur, 2001). These research reports clearly suggested that the increasing metal concentrations significantly reduced the removal efficiency of microorganisms under such harsh environmental conditions. This might have been due to the toxicity of heavy metals that induced various physiological and biochemical changes such as decreased biomass, disturbed cellular functions and deactivation of microbial enzymes (Oves et al., 2016). In general, higher concentrations of heavy metals affect the microbial growth in three different ways: (i) metals may interact with the microbial membrane, which causes irreversible damages in membrane integrity, (ii) absorbed metals in the cytoplasm may inactivate and/or oxidize the cellular enzymes and (iii) heavy metals have the ability to affect the genetic matter of microorganisms by directly interacting with DNA (Fashola et al., 2016; Dixit et al., 2015; Ayangbenro and Babalola, 2017).

**3.2.1.4. Effects of nutrients, organic carbon and O<sub>2</sub>.** Nutrients availability is greatly influenced by both *in situ* and *ex situ* bioremediation rates of microorganisms. Nutrients such as carbon, nitrogen, phosphorus, sulfur, calcium and magnesium are directly involved in microbial growth; they are utilized by microorganisms for metabolic reactions and synthesis of necessary enzymes to break down the contaminants. Optimum concentrations of carbon and nitrogen are very important parameters for microbial growth and metabolism. Carbon is the structural backbone of all organic compounds. Nitrogen is involved in cellular protein and cell wall component synthesis while phosphorous is necessary for cell membrane, nucleic acid and ATP (Xu et al., 2015). Venil et al. (2011) reported that the optimum concentrations of carbon and nitrogen sources in the growth medium significantly induced the chromium removal efficiency of *Bacillus* sp. REP02. Similarly, Maheswari and Murugesan (2009) also reported the influence of various nutrient sources on arsenic bioremediation by *Aspergillus nidulans*. Majority of the microbial heavy metal bioremediation processes involve oxidation. Oxygen is a key factor for bioremediation because it is an energy yielding process and it determines the bacterial pattern.

### 3.3. Climatic factors

Climate change is also an important factor in microbial growth and metabolisms. Conversely, there is no direct indication of climatic influence on microbial bioremediation process. However, several researchers suggested that alterations in the physicochemical nature of the microbial vicinity may change and/or affect the metabolic activities of microorganisms and thereby bioremediation (Nie et al., 2013; Srivastava et al., 2014). Sowerby et al. (2005) reported that the extracellular enzyme production from microorganisms would be related to microbial activity as well as physicochemical properties of the inhabited soil, which were influenced by climatic conditions. Global climatic change is dependent on two major factors, namely, CO<sub>2</sub> concentration and atmospheric temperature. Climatic factor, especially, CO<sub>2</sub> at elevated levels is associated with the increase in bacterial population (Castro et al., 2010) and significant reduction in the population of fungus (Frey et al., 2008). Similar to CO<sub>2</sub> levels, soil temperature also influences microbial growth as well as enzymatic activities. Warm and dry conditions generally proved detrimental to fungal biomass (Sowerby et al., 2005). Photosynthetic efficiency is another important parameter that affects bioremediation. In a recent study, Bwapwa et al. (2017) highlighted the prominent role of photosynthetic efficiency of algae that enhanced the overall heavy metal biosorption. According to Elbaz-Poulichet et al. (2000; Brake et al., 2004), the optimum removal of heavy metals and contaminants by algae vary with the type of season because of parameters such as light and temperatures. Algae are very sensitive when it comes to parameters related to seasons such as temperature and light intensity. Hence, these parameters should be considered to create an efficient bioremediation strategy.

## 4. Role of enzymes in bioremediation

During the bioremediation cascade, the plants and microbes enzymatically attack the heavy metals and neutralize them into non-toxic counterparts (Karigar and Rao, 2011). The potency of biological agents for remediating heavy metals hugely depends on the enzymes that harbor in them. These biocatalysts are known to catalyze the biodegradation of heavy metals via oxidation, reduction, hydrogen ion abstraction, polymerization etc (Chandra and Chowdhary, 2015). The subsequent paragraphs discuss the active roles of major enzymes involved in the bioremediation of organic pollutants.

### 4.1. Oxidoreductases

In the detoxification of toxic organic compounds, oxidative coupling reaction is facilitated via oxidoreductases of different microorganisms and plants (Gianfreda et al., 1999). These enzymes cleave the bonds and consume the energy yielded from biochemical reactions and help out in electron transfer from the reduced organic compound to another chemical compound. By these reactions, harmful contaminants are finally oxidized to harmless compounds. These enzymes also contribute towards the humification of diverse phenolic compounds that occur as a result of lignin decomposition in soil environment. They also detoxify various xenobiotics such as anilinic or phenolic compounds by the way of reactions ie. polymerization, copolymerization with different substrates or via association with humic compounds (Park et al., 2006). Microbial enzymes proved their capabilities in azodye degradation and decolorization (Husain, 2006; Saratale et al., 2011a; Saratale et al., 2016). The plant families ie. Fabaceae, Solanaceae and Gramineae were found to liberate oxidoreductases, which oxidatively degraded certain soil constituents (Gramss et al., 1999). Treatment of phenol contaminated water can be performed via plants and enzymes exuded from their roots (Ruiz and Romero, 2001). For the treatment of chlorinated phenolic compounds from the affected area, different fungal species are considered suitable. These fungal activities are the results of performances of oxidoreductase enzymes ie. manganese peroxidase (MnP), laccase (Lac) and lignin peroxidase (LiP), which are released extracellularly by different fungal mycelia.

#### 4.1.1. Oxygenases

Oxygenases belong to the class of oxidoreductases. Traditionally, in the field of bioremediation, bacterial mono/dioxygenase enzymes are most considered. Their roles in the metabolic processes of organic molecules are central as they enhance the water reactivity/water solubility or assume a key part in the metabolism of organic molecules by enhancing their reactivity/water solubility or piercing of aromatic ring (Gramss et al., 1999; Hayaishi, 2012). Oxygenases work against a versatile range of substrates and are dynamic towards an extensive variety of compounds, which includes chlorinated aliphatics. Oxygenases in combination with multifunctional enzymes also facilitate the dehalogenation reactions against halogenated methanes, ethylenes and ethane etc (Hayaishi, 2012).

#### 4.1.2. Laccases

Among the biological agents, laccases are universal in nature and are found as a fascinating group of oxidoreductase enzymes that have an extraordinary potential in the field of bioremediation and biotechnology. Laccases (*p*-diphenol:dioxygen oxidoreductase) is a family of multicopper enzymes secreted by specific plants, insects and microorganisms, which help in the oxidation of a wide variety of reduced aromatic and phenolic compounds with corresponding shrinking of oxygen into water (Catherine et al., 2016). Laccases are found in the form of multiisoenzymes; each enzyme is encoded by a specific gene. Numerous microorganisms deliver extra and/or intracellular laccases having the capability to catalyze oxidation reactions of various aromatic and nonaromatic compounds (polyamines, aminophenols, lignin, polyphenols, aryl diamines and paradiphenols) along with inorganic ions (Catherine et al., 2016). Laccases also oxidize methoxy-phenolic and phenolic acids, decarboxylate them and perform demethylation involved in the depolymerization of lignin.

#### 4.1.3. Peroxidases

Peroxidase (donor: hydrogen peroxide oxidoreductase) is a

universal enzyme that uses hydrogen peroxide to promote the chemical's oxidation into free radicals, which subsequently enhances the lignocelluloses biodegradation and participate to the bioconversion of diverse recalcitrant compounds (Medina et al., 2017). Classification of peroxidases are on the basis of their higher potentials to degrade toxic compounds released in nature i.e. lignin peroxidase (LiP), manganese-dependant peroxidase (MnP) and versatile peroxidase (VP) (Medina et al., 2017). Peroxidases have the capabilities to treat the wastewater having phenols, cresols and other effluents discharged from the industries, to decolorize dyes, to expel endocrine problems causing chemicals and to efficiently degrade pesticides, polychlorinated biphenyls, chlorinated alkanes and alkenes from the soil, triazine herbicides, phenoxyalkanoic herbicides, chlorinated dioxins and chlorinated insecticides. For sustainable bioremediation, the use of peroxidases for pollutant degradation and environmental protection has been in more light.

Lignin peroxidases are heme proteins (Fujii et al., 2013) generally secreted by the white rot fungi in the secondary metabolism step. Lignin peroxidase (LiP) performs a key part in the biodegradation of lignin, which is found in the plant cell wall. It has the capacity to perform oxidation of aromatic substances with a release of single electron (redox potential > 1.4 V (NHE)) (Karigar and Rao, 2011).

Manganese peroxidase (MnP) is an extracellular heme enzyme released by basidiomycetes fungus, which is lignin degrading in nature, and oxidizes divalent manganese to trivalent through multistep reactions. Mn<sup>2+</sup> serves as a substrate for manganese peroxidases, thus, empowering the manganese peroxidase production. Mn<sup>3+</sup> generated by MnP mediates the oxidation of a variety of phenolic compounds (Karigar and Rao, 2011).

Versatile peroxidases (VP) have the capability to oxidize divalent manganese, methoxybenzenes and phenolic/aromatic compounds as MnP and LiP. Versatile peroxidases have a wide substrate specificity and preferentially oxidize the substrates without manganese in contrast to different peroxidases. Thus, it has been exhibited that versatile peroxidases can oxidize both phenolic and non-phenolic lignin model dimers (Karigar and Rao, 2011).

#### 4.2. Hydrolytic enzymes

Hydrolytic enzymes detoxify various toxic compounds by disruption of different chemical bonds, which in turn reduces their toxicity. Mechanism of this type is handy for the biodegradation of organophosphates, oil spills and carbamate insecticides. Hydrolases also catalyze various reactions, which include condensations and alcoholysis (Vasileva-Tonkova and Galabova, 2014). These enzymes have certain advantages: availability, tolerance of additional water-miscible solvents and lack of cofactor stereoselectivity. In enzyme classification, hydrolases belong to the third group and further divide on the basis of bond hydrolysed.

##### 4.2.1. Lipases

Lipases are ubiquitous in nature and catalyze the hydrolysis of triacylglycerols to glycerol and free fatty acids (Sharma et al., 2011). These lipolytic activities mainly happen at the lipid water interface, where exists an equilibrium between lipolytic substrates and monomeric, micellar and emulsified states. The key constituent of fat is triglyceride, which is successively hydrolysed to diacylglycerol, monoacylglycerol, glycerol and fatty acids. Extraction of lipases from microorganisms, plants cells and animal cells, which catalyze a variety of reactions including hydrolysis, esterification, interesterification, aminolysis and alcoholysis, can be performed. Lipase gains more interest in the production of regiospecific compounds employed in pharmaceutical industry (Margesin et al., 1999).

##### 4.2.2. Cellulases

Cellulases promise the potential of utilizing waste cellulosic biomass and converting it into foods to encounter the growing population needs and thus, considered as a subject of strong research. Several microorganisms have the capabilities to produce cell bound and extracellular cellulases. Cellulases are generally a mixture of number of enzymes (Juturu and Wu, 2014). The major groups of cellulases, which take a part in hydrolysis include the following three: endoglucanase (EG, endo 1,4-D-glucanohydrolase), whose area of attack is the lower crystalline region of the cellulosic fiber, which results into free ends of chain; exoglucanase/cellobiohydrolase (CBH, 1,4-b-D-glucan cellobiohydrolase), which splits cellobiose units from the free ends of cellulosic fiber; β-glucosidase, which hydrolyzes these cellobiose units into monomeric glucose units (Saratale et al., 2012, 2017b). In the process of enzymatic hydrolysis, cellulosic fibers are converted into reducing sugars by the cellulases, which are then fermented to ethanol by some yeast or bacteria. Since 1990s, cellulases have been used in detergent manufacturing industries. Cellulose microfibrils formed during washing are removed by cellulases and are also found to be a colour brightening agent and softeners of textiles. In pulp and paper industry, recycling of paper has been achieved after the removal of ink with the help of cellulases (Karigar and Rao, 2011).

##### 4.2.3. Proteases

Proteases perform the function of breakdown of proteinaceous materials that enter in the atmosphere as a result of death of animals, detaching and shedding of their parts and as well as byproducts of various industries including fishery, leather and poultry. Proteases catalyze the breakdown of peptide linkages in the presence of water and synthesize them in non-aqueous medium (Clausen et al., 2011). Proteases have wide applications in ie. food, detergent, leather and pharmaceutical industries.

Proteases are grouped into endopeptidases and exopeptidases on the basis of catalysis of peptide chains. On the basis of position of active sites, endopeptidases are further grouped as cysteine peptidases, serine endopeptidases, aspartic endopeptidases and metallopeptidases. The exopeptidases attack only on the nearest terminal amino position or carboxylic position within the chain. The aminopeptidase and carboxypeptidase enzymes attack on the free amino and carboxyl ends, respectively. The endopeptidase attacks on the interior sides of the peptide chain. Free amino and carboxyl terminal's presence affects the enzyme activity (Beena and Geevarghese, 2010). Proteases have been extensively used in different industries including cheese, detergent, dipeptide aspartame production (artificial sweetener), pharmaceuticals and leather (for hair removal from animal skin).

#### 5. Phytoremediation

Phytoremediation refers to *in situ* use of plants and their associated microorganisms to degrade, contain or render harmless contaminants in the environment (Ayotamuno et al., 2006). It can be used for the removal of various organic (polynuclear aromatic hydrocarbons, polychlorinated biphenyls, and pesticides) as well as inorganic pollutants (heavy metals) (Rezania et al., 2015). Phytoremediation possesses certain advantages that it is an autotrophic system having a large biomass requiring input of very little nutrients, is simple to manage, and is generally agreed by the society because of its aesthetic appeal and environmental sustainability (Saratale et al., 2011a). Many plant species have the abilities to accumulate various toxic heavy metals into their vegetative as well as reproductive parts. Green plants can modulate the availability of heavy metals without affecting the top soil; thereby stabilizing the soil fertility (Olowu et al., 2015; Ali et al., 2013). Compared with

other traditional techniques, phytoremediation is a valid option as it is economically feasible and eco-friendly. And improves the soil fertility by releasing various organic matters. In general, plants have an enormous ability to take up the heavy metals from the environment by various mechanisms such as phytoextraction, phytofiltration, phytostabilization, phytovolatilization and rhizodegradation (Rezania et al., 2016; Ali et al., 2013). Recently Borker et al. reported the potential of cadmium uptake by aquatic weed *Eichhornia crassipes* and effects of some biochemical parameters including, growth root length, leaf area and biomass production of *E. Crassipes* on cadmium uptake. In addition, they have investigated the effects of increasing concentrations of Cd on chlorophyll, polyphenol and proline contents. The study proved that the species was more favourable to tolerate higher concentrations of heavy metals and could be a better option for the treatment of cadmium by phytoremediation (Borker et al., 2013).

### 5.1. Phytoextraction

Phytoextraction is the uptake of contaminants from the environment by plant roots and accumulation of those contaminants in parts above ground (shoots). It is also known as phytoaccumulation or phytoabsorption (Kotrba et al., 2009). Phytoextraction is the easy and best approach to remove heavy metals primarily from the contaminated soil, without altering soil fertility and structure (Ullah et al., 2015). Phytoextractor plants have multiple traits to tolerate and extract heavy metals from the contaminated environment. The traits are (i) fast growth with high biomass, (ii) extended root system, (iii) easy cultivation, (iv) adaptation to different environmental conditions and (v) repulsion to herbivores (Seth, 2012; Chatterjee et al., 2013). Previously, plants species such as *Brassica juncea*, *Helianthus annuus*, *Thlaspi caerulescens*, *Alyssum* sp., *Astragalus racemosus* and *Sedum alfredii* are identified as hyperaccumulator plants based on their fast growth and maximum heavy metal accumulation efficiencies (Milner and Kochian, 2008; Lu et al., 2008; Deng et al., 2008).

### 5.2. Phytofiltration

Phytofiltration is termed as rhizofiltration since the pollutants are absorbed by the plant roots from the aqueous streams. Phytofiltration is another heavy metal removal approach in phytoremediation with the help of aquatic plants either free floating, submerged or emergent plants (Pratas et al., 2014). In phytofiltration, heavy metals are adsorbed or absorbed by the plant materials and thus, mobility of the contaminants to underground water is minimized (Thakur et al., 2016). In order to extract maximum quantities of heavy metals, phytofiltration plants should grow hydroponically and have dense root systems. Moreover, phytofiltration efficiencies of the plants highly depend on the biochemical characteristics of the plants.

### 5.3. Phytostabilization

Phytostabilization is the process to reduce the heavy metal mobility in the environment by sorption and accumulation in root tissues, precipitation within the root zone or reduction in metal valence in the rhizosphere, rendering them harmless, thus, preventing their entry in to the food chain as well as ground water (Wuana and Okieimen, 2011). Phytostabilization plants have the ability to convert hazardous metal state to a relatively less toxic state by excreting special redox enzymes. Phytostabilization plants contain an extensive root system that provides good soil colonization and easy contact with the heavy metals. Previously, few plant species such as *Agrostis capillaris*, *Festuca rubra* and *Lupinus*

*albus* are identified as potential phytostabilization plants (Kidd et al., 2009; Vázquez et al., 2006).

### 5.4. Phytovolatilization

Phytovolatilization is a type of phytoextraction, where heavy metals are not permanently accumulated in the aboveground biomass but instead get converted to the less toxic volatile form and subsequently released into the atmosphere (Chatterjee et al., 2013). Phytovolatilization is a promising technique for the removal of mercury (Hg) and selenium (Se), in which these heavy metals are converted to volatile forms and released into the atmosphere through the leaves or foliage system. Sakakibara et al. (2010) reported around 90% phytovolatilization of Arsenic from the soil by *Pteris vittata*. Moreover, phytovolatilization process has advantages than other phytoremediation techniques, as it removes metal (metalloid) from the contaminated environment without the need for harvesting and disposal of heavy metal accumulated plants.

### 5.5. Rhizodegradation

Rhizodegradation refers to the reduction/conversion of heavy metal ions in the rhizosphere by rhizospheric microorganisms (Tangahu et al., 2011; Ullah et al., 2015). The increased metal reduction in rhizospheric region may be due to the increased metabolic activities in rhizospheric region. In rhizosphere, plants can increase microbial activities about 10–100 times by the production of root exudates containing sugar, amino acids, flavonoids, etc. These plant derived root exudates provide carbon and nitrogen sources to the rhizospheric microorganisms and create nutrient rich environment, which leads to the increased microbial activity. Rhizospheric microorganisms have the ability to produce various chelating agents such as siderophores, biosurfactants, gluconic acid, oxalic acid and citric acid, which play key roles in heavy metal mobilization and transformations (Gadd, 2010; Rajkumar et al., 2012). For instance, siderophore producing rhizobacterial strains significantly increased the bioavailability of Cr and Pb in rhizospheres and made them available to the plant (Braud et al., 2009). Similarly, Saravanan et al. (2007) also reported that organic acid producing *Gluconacetobacter diazotrophicus* had the ability to solubilize Zn compounds. Moreover, rhizobacterial strains have developed various reduction/oxidation mechanisms against heavy metals. Solubility of Fe(III) and Mn(IV) have been increased by reduction of Fe(II) and Mn(III), respectively (Gadd, 2010).

## 6. Immobilization techniques in bioremediation

Immobilization of biosorbents is a very useful technique in industrial applications where large amounts of heavy metal contaminants are required to be treated. The multipolluted soil cannot be bioremediated easily since the process applied can result in confiscatory effects on the mobilization or immobilization of various pollutants and heavy metals, which will often decrease the degradation of organic pollutants by microorganisms (García-Delgado et al., 2015; Zhou et al., 2010). Immobilization of cells has been considered as an alternative technology for various environmental applications. Immobilized whole cells deem to be advantageous than freely suspended cells because of improved mechanical strengths, production of high biomass, effective biosorbent restoration, easy separation of solid-liquids and greater bacterial cell density (Huang et al., 2015; Taqieddin and Amiji, 2004).

Immobilization process can be performed using various materials such as sodium alginate, polyacrylamide, polysulfone, cellulose, polyvinyl alcohol (PVA) and carboxymethylcellulose (CMC)

(Dhanarani et al., 2016; Saratale et al., 2011b). Sodium alginate has been extensively used for immobilizing oil degrading microorganisms. Various carriers have been used to improve microbial degradation; sodium alginate beads delay the exchange of gases, which in turn decreases microbial degradation aerobically (Zhou et al., 2010). Cells of *Bacillus cereus* were immobilized on alginate in a sequential bioreactor to study mercury removal from synthetic effluent (10 mg/L of Hg) and the removal efficiency was 104.1 mg/g on the third day (Sinha et al., 2012). In a batch system, cells of *Desulfovibrio desulfuricans* were immobilized using zeolite for the removal of Cu, Cr, and Ni from contaminated seawater and it showed the removal efficiency of 98.2, 99.8, and 90.1 mg/g, respectively (Kim et al., 2015).

Hence, it is necessary to select the carrier material for enhanced microbial degradation process. In *in situ* bioremediation, the carrier employed should be eco-friendly, since it is difficult to recover the immobilized agent after incorporation into soil or water. Alginate has been used for the removal or recovery of heavy metals and it is a highly promising material because of its low cost, wide availability and high affinity towards heavy metals via gelation (Wang et al., 2014).

## 7. Nanoparticles in bioremediation

Recent years have witnessed a surge of nanotechnology in all walks of human life. Nanoparticles claim a higher surface to volume ratio and hence, have found wide applications in water treatment, catalysis, biosensing and pollutant degradation. In line with these advancements, scientists working on bioremediation have also reported various combinatorial approaches that integrate nanotechnology with bioremediation to eventually enhance the bioremediation efficiency (Mukherjee et al., 2017). The combined efforts have paved way to the terminology- Nanoremediation, the involvement of nanoparticles for remediating heavy metal toxicity. In general, microbial bioremediation has been found ineffective for high metal concentrations, as these elevated concentrations prove lethal to the remediating organisms (Rizwan et al., 2014). In this scenario, integrating nanoparticles with the microbial cells offer an immense potential in the cleaning up of contaminated environment due to their potent reactive sites that may come in contact with the contaminants and hence, result in rapid reduction by detoxification or immobilization (Tratnyek and Johnson, 2006).

Literature suggests that metal nanoparticles synthesized chemically in the laboratory have been integrated to biological agents like enzymes and whole cells to aid bioremediation of various pollutants. Li et al. (2007) reported that integrating bioremediating enzymes like peroxidases to iron/magnetite nanoparticles resulted in an increased enzyme stability and activity against the pollutant substrates. Further, magnetite embedded enzymes could also be easily separated from the treatment sites for effective reuse. Further, in another report, palladium nanoparticles were deposited on the cell wall of *Shewanella oneidensis* to result in effective remediation of polychlorophenol residues (Windt et al., 2006). Nanoparticles can be further used to immobilize microbial cells like *Pseudomonas* that can degrade or biorecover specific chlorinated chemicals. It is also noteworthy that various dyes like methylene blue and methyl orange were degraded by biologically synthesized gold and silver nanoparticles (MeenaKumari and Philip, 2015). Therefore, the advantages of nanoremediation are that it decreases the toxic effects of heavy metals on microorganisms, improves the microbial activity towards specific contaminants, eventually, reducing the time needed for remediation and hence, the overall costs.

## 8. Conclusion

Anthropogenic activities such as mining, smelting operations, industrial and domestic, agricultural use of metals and metal containing compounds are the major contributors of heavy metals that result in environmental contamination and subsequent human exposure. Numerous physical, chemical and biological methods have been extensively used for their effectiveness in the removal of metals from different environmental media. Among these methods, biosorption is considered as an innovative technology and remedial strategy to remove the contaminants in view of its cost effectiveness and ecofriendly nature. Microbial systems, characterized by high surface to volume ratios are considered as superior bioremediation agents. Moreover, the microbial membranes harbor abundant potentially active chemisorption sites and hosts multiple functionally and structurally different proteins that aid redox reactions in the bioremediation process. The effectiveness of microbial bioremediation also depends on various biotic and abiotic factors. The microbial enzymes like reductases, oxygenases etc., also influence the process of bioremediation. Phytoremediation, a process involving bioremediation by plants has also emerged as an alternative technology for the management of toxic chemicals. Cell immobilization is a well known technique, which increases the performance of metal uptake from the contaminated environment. An accelerated research interest in this field has resulted in the exploration of nanoparticles for augmenting the properties of biomaterials to tackle heavy metal stress. The extensive review of the literature available in bioremediation indicates that genetic engineering of the biosorbents to improve their heavy metal sorbing properties, the utilization of biomaterials left out after commercially important production processes for biosorption and the fate of the biosorbed materials as growth enhancing factors are still largely unexplored and offer scope for future research.

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