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CHAPTER
[10]

Remediation of heavy metals using non-conventional adsorbents and biosurfactant-producing bacteria

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ABSTRACT

Heavy metal pollution in the ecosystem has attracted worldwide attention due to the persistent non-biodegradable toxic nature that affects not only human beings but also animals and vegetation. Instead of using available conventional techniques, the focus has been shifted to utilize eco-friendly, cost-effective, integrated remediation approaches that are simple, non-conventional with design flexibility and does not harm the prevailing surroundings. The main approaches utilized for remediation of heavy metal contaminated soils are sand capping or land filling, phytoremediation, bioremediation, washing, electro-chemical remediation, stabilization, soil replacement, phytoextraction, phytovoltalization, etc., but again they have their own merits and demerits. Many treatment technologies are employed at industrial scale for HM removal from wastewater effluents such as chemical precipitation, flocculation, coagulation, solvent extraction, adsorption, complexation, electro-kinetics, membrane filtration, etc. Therefore, the present chapter critically highlights the role of non-conventional adsorbents and bacterial surfactants as the best alternative technique for heavy metal remediation from contaminated soil and water systems.

KEYWORDS Adsorbents, Bio-surfactants, Environmental sustainability, Heavy metals

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Introduction

The industrial processes/discharge and natural weathering are the two main causes of heavy metal (HM) pollution due to which the latter are dispersed into land and water ecosystem leading to environmental pollution. The gradual acclimatisation of these soluble metal ions above their permissible limits and their accumulation in the food web exerts adverse toxic and malignant effects on the living forms (Kumar *et al.*, 2019). These HM ions are persistent and can cause their effect even at very low concentrations. HM toxicity directly affects the normal functioning of the body. Lead (Pb) and Cadmium (Cd) are considered as one of the two deadliest HM ions whose persistence over a long period of time can affect central nervous system, can cause damage to vital organs such as lung and kidneys. The main sources of Pb and Cd are paint and pigment industries, electroplating and battery industries. Cd is also released into the environment as a by-product during smelting of Pb and Zinc (Zn) (Dinis and Fiuza, 2011). Mercury (Hg) being another toxic HM ion is discharged through minings, volcanic eruptions, pharmaceutical industries, etc. whose high concentration can affect immune system leading to abnormal brain functioning (Rastogi *et al.*, 2019; Mahmud *et al.*, 2016). Table 1 discusses about some of the common heavy metal ions, source of discharge, permissible limits in different ecosystem and their harmful effects.

Many treatment technologies are employed at industrial scale for HM removal from wastewater effluents such as chemical precipitation, flocculation, coagulation, solvent extraction, adsorption, complexation, electro-kinetics, membrane filtration, etc. (Mohammed *et al.*, 2015) but these are conventional approaches and have their own limitations which are discussed in the coming section (Table 2). The main approaches utilized for remediation of heavy metal contaminated soils are sand capping or land filling, phytoremediation, bioremediation, washing, electro-chemical remediation, stabilization, soil replacement, phytoextraction, phytovoltalization, etc. (Koptsik, 2014; Kumar *et al*., 2019) but again they have their own merits and demerits. The focus has been shifted towards assessing non-conventional approaches or materials to remediate such noxious HM ions from the environment.

Conventional approaches and their limitations

The era of wastewater treatment has given birth to many physico-chemical conventional approaches that has been raised to an alarming rate leading to the generation of secondary toxic sludge/by-products, requires large operational cost and expensive chemicals plus can work efficiently at high concentrations only due to which more attention is diverted towards non-conventional approaches or employing conventional approach using non-conventional methods

Table 1. Sources of heavy metals, types, their permissible limits, and harmful effect on living and non-living system.

Heavy metal	**Sources**	**Permissible limit in soils (mg/kg) adapted from Deuel and Holliday (1994)**	**Permissible limit in drinking water (mg/L) ; WHO standards**	**Toxic effect**	**References**
Cd	Electroplating, Pigmented products, mining etc.	0.01-0.7	0.005	Damage to liver, kidneys, hypertension, carcinogenic	Pavon *et al*. (2019); Das and Al-Naemi (2019)
Cu	Wood processing industries	2-100	1.0	Dermatitis, chronic asthma, generation of free radicals	Alak *et al*. (2019)
As	Wood processing industries, through herbicides, mining, etc.	1-50	0.05	Visceral cancers, kidney and vascular disease,	Navasumrit *et al*. (2019)
Pb	Paint and pigment industries, batteries, automobiles, etc.	2-200	0.05	Damage to brain, fetus, liver, kidneys, bones,	Chung *et al*. (2019)
Zn	Electrolysis, Galvanization processes, paints, fertilizers, etc.	10-300	5.0	Nervous sytem dysfunction, growth retardation	Poole *et al*. (2019)
Hg	Soil leaching, fossil fuel burning, etc.	0.01-0.3	0.001	Circulatory and nervous system disorders,	Cariccio *et al*. (2019)
Fe	Smelting, fertilizers, mining, etc.	7000-550,000	0.1	Retarted growth, low RBC count	Hino *et al*. (2019)

Table 2. Merits and demerits of common conventional approaches of wastewater treatment.

Technology	Heavy metal	Advantages	Disadvantages	References
Chemical precipitation	Cu(II), Zn(II), Cd (II), Pb(II)	Cheap and Simple method	Sludge generation, costly, can't detect low metal ion concentration	Huang *et al.* (2019); Wu (2019)
Ion exchange	Pb(II), Cu(II), Ni (II)	Regeneration of resins is possible	Expensive, secondary pollutant generation	Nemati *et al.* (2019); Ma *et al.* (2019)
Coagulation/ Flocculation	Pb(II), Cd(II), Cu (II), Cr(III), Ni (II), Co(II), As (III)	Sludge settling characteristics	High chemicals input and maintenance	Bora and Dutta (2019)
Membrane filtration	Zn(II), Cd(II), Pb (II) , Hg(II)	Highly efficient	A complex and costly method	Ye *et al.* (2019); Efome *et al.* (2019)
Floatation	Sr(II), La(III), As (V)	Selectivity, efficiency	High maintenance and operational conditions	Elazzouzi *et al.* (2019); Taseidifar *et al*. (2019)
Electro-chemical treatment	Cd(II), Pb(II), Zn (II)	Fast and controlled process	High operational cost	Giwa *et al*. (2019); Delil *et al*. (2020)
Adsorption	Cr(VI), Zn(II), Pb (II), Cd(II), Cu(II)	Cost effective by using low cost adsorbents, Biosorption-a new vista in adsorption technology	Process efficiency depends on type of adsorbent used	Kyzas *et al.* (2019); Sharma *et al*. (2019)

or materials (Rangabhashiyam *et al*., 2019). However, the advantage and disadvantages of some of the common conventional approaches have been summarized in Table 2.

Sustainable amendments for heavy metal remediation

Adsorption

Among all the conventional approaches available for remediation of heavy metals, adsorption is the most appropriate ancient technology as it is simple to perform, requires less operational cost and has design flexibility. C.W. Scheele in 1773 showed first time the uptake of gases onto charcoal and clays (Bhatnagar and Minocha, 2006) but the term 'Adsorption' was coined by a German physicist Heinrich Kayser in 1881 (Calvert, 1990). It is defined as a surface phenomenon which involves adherence or binding of a chemical species (known as adsorbate) on to the solid or liquid surfaces termed as adsorbent (Crini *et al*., 2019). An adsorbent is selected on the basis of its pore size (surface porosity), high surface area and surface chemistry and the type of pollutant in study (Bhatnagar and Minocha, 2006).

Heavy metal remediation using non-conventional adsorbents

The usage of commercial activated carbons (CACs) or materials that are being converted into ACs are being restricted due to their expensive operational and manufacturing cost and attention has been shifted towards application of cost effective non-conventional adsorbents (NCAbs). These NCAbs could be of biological origin or from natural materials and can be applied directly in their raw or treated form (Crini *et al*., 2019). Their application has been increased at an alarming rate in the past few years as they are abundant in nature, are economical ready to use (or can be modified) but their usage is still restricted to pilot scale and needs to be explored more in large field applications (Sangeetha *et al*., 2017).

Agricultural solid wastes as adsorbents/ nonconventional green adsorbents: In recent years, agricultural solid waste (ASW) has been explored at various levels in their natural or modified form using physico-chemical methods for pollutant removal as former mainly composed of lignin, hemicellulose, lipids, hydrocarbons, carbohydrates, proteins, water that contain various functional groups on their surfaces (Gisi *et al*., 2016). These functional groups present on their surfaces have charges that can facilitate binding of a particular pollutant by varying pH levels (Rastogi *et al*., 2019). Rosales *et al*. (2019) investigated the role of untreated lime peel and pineapple core wastes in the removal of Cr (VI) from aqueous solutions with adsorption capacities of 9.20 and 4.99 mg/g respectively at pH 2.01. In an another recent study conducted using peels of *Artocarpus nobilis* for the removal of Ni(II) showed enhanced metal removal efficiency from 50 to 71 to 93% through optimization processes having 12,048 mg/kg as maximum adsorption capacity via static and dynamic conditions with Freundlich model as the best fitted adsorption model where regression coefficient has 0.994 value (Priyantha and Kotabewatta, 2019). An efficient adsorption process includes optimization of various factors that can affect an adsorption study such as pH, adsorbent dose, reaction contact time, initial metal concentration, temperature, revolutions per minute (rpm), pressure, etc. which are needed to be identified for the large scale application of adsorption process (Guyo *et al*., 2017). Biswas *et al*. (2019) employed central composite design (CCD) for adsorption factors optimization using a novel biochar aliginate composite adsorbent in the removal of Zn(II) ions. They reported the initial Zn(II) concentration (43.18 ppm) and adsorbent dose (0.062 g) as most effective factors on account of high f-value which explained maximum adsorption capacity of 120 mg/g giving 85% removal efficiency. Though the conversion of agricultural waste residue at nano-scale level provides high surface area but also leads to difficulty in their separation from the study system, therefore, focus has been shifted to utilise them in the dual form where an adsorbent is merged with a suitable membrane (Zeng *et al.*, 2016). Hubadillah *et al.* (2016) explored the efficiency of green ceramic hollow fibre membrane (CHFM) synthesised from rice husk ash (RHA) in removal of Ni(II), Zn(II) and Pb(II) ions giving 99% removal rate. The modified CHFM/RHA based dual function material and others might serve as a promising low-cost adsorbent + filtration unit for the removal of noxious heavy metal ions from the aqueous systems.

Industrial by-products as low-cost adsorbents: The processing of substances at industrial level generates huge amount of secondary wastes whose disposal is another problem but these can be utilised as adsorbents in their raw or modified form. For instance, the iron industry during smelting of iron in blast furnace produces slag waste whereas coal industry generates fly ash wastes that can be optimized for heavy metal removal from waste streams. Nguyen and his team assessed the removal efficiency of slag and fly ash wastes in the removal of five metals (Pb, Cu, Cd, Cr and Zn) and found the maximum adsorption capacity for Pb and Cd, when used in multiple metal system at an optimum pH 6.5 (Nguyen *et al.*, 2018). Another mixed metal system study conducted by Ma *et al.*, (2018) reported the maximum adsorption capacities to be 420.17, 680.93, 251.89, and 235.29 mg/g for Ni(II), Cu(II), Zn(II) and Co(II) respectively using a novel waste product 'calcium silicate powder' as adsorbent obtained during alumina production in coal ash industry. Liu *et al.* (2017) employed fly ash based granular adsorbent containing zero valent iron (ZVI-GAM) for the removal of Pb(II) and Cr(VI) from the aqueous system with 78.13 and 15.70 mg/g maximum adsorption capacities respectively. Red mud is another waste by-product that is being exploited as an efficient adsorbent. Hydrazine sulphate mixed red mud when incorporated in calcium alginate beads utilised as an excellent adsorbent for Pb(II) ions removal having 138.6 mg/g adsorption capacity (Babu *et al.*, 2017). Tsamo *et al.* (2018) explored the efficiency of low cost raw and hydrocholoric acid treated red mud in the removal of Cr(VI), Cu(II) and Pb(II). They reported that acid treated red mud had only little affect in removal of Cr(VI) and Cu(II) but had increased removal percentage for Pb(II) (79.365 from 52.083 µmol/g adsorption capacity). Ahsaine *et al.* (2017) reported the use of sulphuric acid modified sewage sludge for the removal of Cd(II) ions from aqueous system with adsorption capacity of 56.2 mg/g. A similar study explored the role of thermally (physical activation) modified sewage sludge in the removal of Cu(II) giving about 73% removal rate from the synthetic wastewater (Abdel-Aziz *et al.*, 2017). In the recent years, many researchers have worked with industrial wastes as suitable adsorbents for the heavy metal removal.

For instance, iron ore slime (a mining waste) for Pb(II) and Hg(II) removal (Sarkar *et al.*, 2017); carboxymethyl-chitosan treated solid sludge biochar for Pb(II) and Hg(II) ions (Ifthikar *et al.*, 2018); coal fly ash for Hg(II) removal (Attari *et al.*, 2017); magnetic 4A-zeolite from red mud for Al (III), Fe(II), and other metals (Xie *et al.*, 2018). Recently, hollow porous granules (PS-HPGs) were synthesised from industrial wastes of polysulphone hollow fibre membranes when incorporated with nano-range polydopamine (PD) served as efficient adsorbent for the 80% removal of Cu(II) ions and for Zn(II) and Ni(II) ions after certain modifications (Posati *et al*., 2019).

Natural materials: It is usually advocated that mesoporous adsorbents derived from natural materials are good candidates for the heavy metal removal study as these provide large surface activity due to large surface area and uniform large pore size. Mesoporous silica materials (MSMs) derived from MCM41 type was investigatd in the removal of Cu(II), Cd(II) and Pb(II) with adsorption capacities around 36.3,32.3 and 58.5 mg/g in the pH range 5-7 (Zhu *et al*., 2017). Vojoudi *et al.* (2017) evaluated the efficiency of magnetic mesoporous silica as nanoadsorbent for the removal of Pb(II) and Hg(II) ions in batch study leading to 303.03 and 256.41 mg/g adsorption capacities respectively.

Microbial bioadsorbents: The utilization of microorganisms in the eradication of toxic pollutants from contaminated environment is known as bioremediation. Their inbuilt biosorptive or bioaccumulative mechanistic ability (Javanbakht *et al*., 2014) helps them to tolerate heavy metal toxicity that can be employed in many ways such as absorption, adsorption, oxidation, etc. in pollutant removal or in restoration of original environment (Rajendran *et al*., 2003). Also, these microorganisms either bacteria, fungi or alga are being exploited in their live as well as dead form that makes them as potential biosorbing agents for the sequestration of heavy metal ions from the aqueous environments (Ayangbenro and Babalola, 2017). Jaiswal *et al.* (2018) used alginate beads immobilized with fungal biomass as biosorbing material in the removal of As at pH 6 and found the adsorption capacity of about 59.5 mg/g. The potential of dried *Gelidium amansii* (marine alga) biomass in free and immobilized form was assessed for the removal of Pb(II) leading to 100% removal percentage at pH 4.5 (El-Naggar *et al*., 2018). Jin *et al.* (2017) investigated the potential of bacterial cellulose pellicles modified with polyethyleneimine in the removal of Cu(II) and Pb(II) ions with maximum adsorption capacities to be 148 and 141 mg/g respectively. Microorganisms are being used not only as whole in live or dead form as adsorbents but their secretions are also explored as suitable adsorbents for the removal of toxic metal ions from waste streams. Castro *et al.* (2018) explored the efficiency of biogenic (bacterial) iron compounds mainly siderite and magnetite as adsorbent in the removal of Cu, Zn, As, and Cr and reported higher removal percentage for As in single and bimetal system (As-Cu). Li and Zhou (2018) used heavy metal resistant immobilized *Brevibacterium* as bioadsorbent for the removal of Pb and Cd having 114.36 and 82.12 mg/g maximum adsorption capacity. A brief overview of various non-conventional adsorbents has been summarized in Table 3.

Nanoadsorbents/nanocomposites: The applicability of adsorbents that are carbon-based or metal oxide and metal organic frameworks (MOFs), zeolites in the nano-range has been increased in the recent years due to their large surface area and high surface chemistry (Nasir *et al*., 2019). Zanin *et al*. (2016) assessed the role of natural clinoptilolite zeolite (CL) as adsorbent in the

Table 3. Explains various examples of non-conventional adsorbents, target heavy metal ion(s) and their adsorption efficiency.

Non-conventional adsorbent type	**Example**	**Target heavy metal ion(s)**	**pH**	**Adsorption capacity (mg/g)**	**References**
Nanocomposites/ Biocomposites	Chitosan-boehmite desiccant composite	Pb(II), Cd (II), Hg(II)	6-7 (Pb(II), Cd (II) & 10 (Hg (II)	98.84, 99.54, 74.98	Rajamani *et al.* (2019)
Nanocomposites/ Biocomposites	Cellulose biocomposite sponge	Hg(II)	5.5	495	Zhang *et al.* (2019)
Nanocomposites/ Biocomposites	Fe3O4@BHPS	Pb(II), Cd (II)	5.5, 7.1	186.2, 125	Alqadami *et al.* (2019)
Nanocomposites/ Biocomposites	SiO2@chitosan composite	As(V), Hg (II)	6-7	198.6, 204.1	Liu *et al.* (2019)
Agro-Industrial wastes	Zeolite from JIS type II fly ash	Hg(II), Pb (II)	5	30.8, 40.5	Kobayashi *et al.* (2020)
Agro-Industrial wastes	Carboxymethylated softwood kraft pulp cellulose fibers	Cu(II), Ni (II)	6	16.90, 11.63	Wang *et al.* (2019)
Agro-Industrial wastes	Lemon peel	Cu(II)	3	13.2	Meseldzija *et al.* (2019)
Agro-Industrial wastes	Acid modified Biochar from rice husk	Cr(VI)	2	4536µg/g	Sarkar *et al.* (2019)
Microbe based/ Microbial bioadsorbent	Bacterial cellulose/ attapulgite magnetic composites	Cu(II), Cr (VI), Pb (II)	5.5	70.5, 91.0, 67.8	Chen *et al.* (2020)
Microbe based/ Microbial bioadsorbent	Graphene oxide based bacterial cellulose	Cu(II), Cd (II), Pb(II)	5-5.5	91.32, 148.37, 160.0	Luo *et al.* (2020)
Microbe based/ Microbial bioadsorbent	*Pseudomonas* sp. strain 375 (live and dead form)	Cd(II)	7	92.59, 63.29	Xu *et al.* (2020)
Microbe based/ Microbial bioadsorbent	*Penicillium* sp.	Pb(II)	5.5	0.16	Rastogi *et al.* (2019)
Microbe based/ Microbial bioadsorbent	*Pseudomonas* sp. strain DC-B3	Cu(II), Cd (II)	6	12.6, 26.5	Liang *et al.* (2019)
Industrial byproducts	Graphene oxide based newspaper wastes	Pb(II), Ni (II), Cd(II)		75.41, 29.04, 31.35	Chen *et al.* (2020)
Industrial byproducts	Incinerated sewage sludge ash	Pb(II)	6	62.42	Wang *et al.* (2019)
Natural materials	Magnetic Fe_3O_4-chitosan@bentonite	Cr(VI)	2	62.1	Feng *et al.* (2019)
Natural materials	Clay minerals (bentonite, volcanic ash soil, red soil)	Ni(II), Cu (II), Zn(II)	-	99.9, 99.9, 89.2	Esmaeili *et al.* (2019)

removal of heavy metals from graphic industry with removal efficiency up to 95.4, 96.0 and 85.1% for Fe, Cu and Cr respectively. But these nanocomposites tend to agglomerate that results in reduction of surface area, also gives rise to recyclability and environmental issues due to which these are utilized in hybrid composite forms (Bajpai *et al*., 2019). Shahat *et al.* (2015) explored the role of an organic nano-ligand N, N'-di (3-carboxysalicylidene)-3, 4-diamino-5-hydroxypyrazole that was anchored using building block approach on mesoporous silica and termed as facial adsorbent for the removal of Co(II) ions from their aqueous solutions and reported maximum adsorption capacity of 157.73 mg/g at higher pH values. In an another similar study conducted by Vafaeifard *et al.* (2019) analysed the potential of nanostructured flowerlike $Mg(OH)_2$ that was assembled on granular polyurethane as nanoadsorbent for the removal of Cu (II), Cd (II) and Pb (II) with astonishing 472, 1050 and 1293 mg/g adsorption capacities respectively in batch processes and up to 184 mg/g adsorption capacity for Cu(II) in a continuous-flow column study. Bio-nanocomposites are advantageous as they impart biodegradability, biocompatibility and antimicrobial activity (Bajpai *et al*., 2019). Souza *et al*. (2018) investigated the potential of *Malpighia emarginata D.C.* seed fibers microparticles (Me-SFMp) as bioadsorbent and found metal removal efficiencies up to 81, 84.2, 86.8, and 95.1% for Ni, Cu, Pb and Cr respectively while 100% for both Zn and Cd. An efficiency of a novel chitosan-iron (oxyhydr) oxide composite known as chitosan goethite bionanocomposite (CGB) in the form of beads was explored and found to remove As(V) more than As(III) from aqueous solutions through diffusion-adsorption mechanism (He *et al*., 2016). Ahmad and Mirza (2015) evaluated the role of methionine modified bentonite/alginate (Meth-bent/Alg) in the removal of Pb(II) and Cd(II) at pH 5 and 4 respectively with 30.86 and 217.39 mg/g adsorption capacities at 303 K respectively.

Polymer-layered silicate nanocomposites (PLSNs) and polymer-functionalized nanocomposites (PFNCs) are emerging as superior nonconventional nanocomposites as these provide stability, better reinforcement rate at less than 10%, resistance against many solvents, temperature, ions and have mechanical strength, diverse functional groups on their surfaces leading to strong specific bindings to metal ions or any other pollutant (Ucankus *et al*., 2018; Bajpai *et al*., 2019).

Bacterial bio-surfactants

The unfavourable environment triggers a stress response in microorganisms such as bacteria and fungi to produce various secondary metabolites to cope up with those antagonistic conditions. Bacterial bio-surfactants are one such compound that has proved their existence fruitful for the bioremediation of inorganic contaminants particularly heavy metals (Akbari *et al*., 2018). Table 4 explains about different class of biosurfactant and their types along with latest metal remediation potential. Some of the common properties that make a bio-surfactant molecule to be preferred over chemical surfactants are surface and interfacial tension reduction ability, highly tolerant to

Table 4. Bio-surfactant class/type producing microorganism and their action on metal ion type with removal method (adapted from Sarubbo *et al*., 2015)

Bio-surfactant class	**Bio-surfactant type**	**Microorganism**	**Target heavy met al**	**Remediation method**	**References**
Glycolipids	Rhamnolipids	*Psuedomonas* sp., *Shewanella* sp.BS4, *Marinobacter* sp.	Cd(II), Ni(II), Cu(II)	Washing	Shen *et al.* (2019); Lee and Kim (2019)
	Sophorolipids	*Candida* sp. AH62, *C. bombicola* ATCC 22214	Cu(II), Zn(II)	Washing	Da Rocha Junior *et al.* (2019)
	Trehalolipids	*Rhodococcus* sp.	Co(II)	Washing	Narimannejad *et al*. (2019)
	Mannosylerythritol lipids	*Ustilago* sp., *Moesziomyces antarcticus*	-	-	Bakur *et al*. (2019)
Lipopeptides and Lipoproteins	Lichenysin	*Bacillus* sp.	Cu(II), Pb(II)	Washing	Saleem *et al.* (2019)
	Surfactin	*Bacillus subtilis, paenibacillus* sp. D9	Pb(II), Cu(II), Zn(II), Fe(II), Ca(II), Ni(II), Cr(VI), Cd(II)	Washing	Jimoh and Lin (2020); Hisham *et al*. (2019)
	Carbohydrate-lipid-protein	*P. fluorescens*	Cr(VI)	Washing	Kalaimurugan *et al*. (2019)
	Mannan-lipid-protein	*C. tropicalis*	Cu(II), Zn(II), Pb(II), Cd(II)	Biosorption	Mbachu *et al*. (2019)
Particulate surfactants	Vesicles	*Pseudomonas marginalis*	Cd(II)	Plant growth promoting phytoremediation	Shahid *et al*. (2019)
	Whole microbial cells	*Cyanobacteria*	Cd(II), Cu(II), Pb(II)	Biosorption	Delneuville *et al*. (2019)

pH, salinity, temperature moderations, biodegradability and biocompatibility, less toxic, specificity and emulsification capacity (Usman *et al*., 2016). There has been done much work in the recent years that has proved the role of bio-surfactant producing bacteria in the bioremediation of heavy metal contaminated soils. Chen *et al.* (2017) assessed the potential of bio-surfactant rhamnolipid in washing of heavy metal ions from river sediment. A dose of 0.8% rhamnolipid removed Cu (80.21%), Cd (86.87%), Pb (63.54%) and Cr (47.85%) after 12 h at pH 7.0. They emphasised that the efficiency of washing depended on initial heavy metal ion speciation, rhamnolipid concentration, washing time, liquid/solid ratio and pH. In an another experimental setup, researchers modified the conventional electro-kinetic treatment with biodegradable rhamnolipid and complexing agent Tetrasodium of N, N-bis (carboxymethyl) glutamic acid (GLDA) in heavy metal removal from sewage sludge and showed significantly higher removal percentages of 70.6 ± 3.41%, 82.2 ± 5.21%, 89.0 ± 3.34%, 60.0 ± 4.67%, 88.4 ± 4.43% and 70.0 ± 3.51% for Cu, Zn, Cr, Pb, Ni and Mn respectively (Tang *et al*., 2017). Similar studies performed by Yang *et al.* (2018) proposed an efficient bioleaching technique using bio-surfactants from *Burkholderia* sp. Z-90 in combination with flocculation by poly aluminium chloride (PAC) as a cost effective, environment-friendly remediation model for severely heavy metal contaminated soils. Their results showed removal efficieny of Zn, Pb, Mn, Cd, Cu and As upto 44.0, 32.5, 52.2, 37.7, 24.1 and 31.6% respectively at 1:20 (w/v) soil liquid ratio for 5 days which were found to be more efficient than that by 0.1% of rhamnolipid. The bioremediation potential of bacterial bio-surfactants pertains to their high biodegradable nature, low toxicity, multi-functionality, environmental compatibility and economical production which make them an excellent alternative over various synthetic surfactants that are available in the market (Akbari *et al*., 2018).

Bio-surfactant mediated methods for the management of heavy metal contaminated soils

There are various methods available for remediation of heavy metal contaminated soils. The different in-situ approaches include surface capping, encapsulation, electro-kinetic extraction, soil flushing, chemical immobilization, bioremediation and phytoremediation and ex-situ methods are landfilling, solidification, soil washing and vitrification (Liu *et al*., 2018; Kumar *et al*., 2019) but bio-surfactant producing bacteria manages this high density metal pollution through soil washing and soil flushing methods (Ayangbenro and Babalola, 2018).

Soil flushing: This is an in-situ approach where a small quantity of biopolymer is injected in the contaminated soil in a cement mixer that has drain pipes or trenches for the introduction and collection of biopolymer solution into or out of the soil. This surfactant based flushing technique was first demonstrated by Pankow and Cherry (1996). The complex thus formed due to the strong bonding between anionic bio-surfactants and cationic heavy metal ions is flushed out of the mixer as it easily separates out from soil matrix and soil gets deposited back into it. The metal

-biopolymer complex precipitates out the biopolymer leaving behind the metal ion (Mulligan *et al.*, 2001; Ayangbenro and Babalola, 2018). Wang and Mulligan (2009) did column experiments to assess the potential of rhamnolipid JBR425 and found enhanced removal of As(V), Cu, Zn and Pb using 0.1% rhamnolipid with 70 pore-volumes flushing operation under alkaline conditions. The desorption of adsorbed metal ions from the adsorbent matrix can be enhanced by flushing the matrix with bio-surfactant-foam solution as demonstrated by Haryanto and Chang (2015) in removal of adsorbed Cu(II) ions from sand-packed columns.

Soil washing: This ex-situ remediation technology eliminates obnoxious heavy metal ions from the soil through washing and scrubbing of the soil with bio-surfactant solution (Sarubbo *et al.*, 2015). Diaz *et al*., (2015) assessed Fe and Zn removal from contaminated soil using alternate cycles of bioleaching with oxidising bacteria (*Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans)* and washing with rhamnolipid solution and found the combined strategy to enhance removal percentage up to 36% for Fe and 63 % to 70% for Zn than alone treatments. The high percentage of toxic contaminants in the soil and sludge may obstruct nutrient recycling and land usage. The washing of soil sediments with bio-surfactant solution could provide a suitable bioremediation alternative that can enhance mineral availability and land application. Tang *et al*. (2019) showed increased metal mobility, binding ability and removal efficiency of Cu, Zn, Cr, Ni and Mn up to 62 %, 74 %, 60 %, 68 % and 64 % respectively than Pb (only 15 %) using rhamnolipids and saponins in multiple washing steps.

Mechanism of heavy metal removal by bio-surfactants

The working strategy for BS mediated HM remediation is based on Le Chatelier's principle either through precipitation or adsorption. BSs are capable of forming complexes with free metal ions present in the solution leading to desorption of metal ions (Wu *et al.*, 2017) from the solution phase. Qi *et al.* (2018) assessed the removal of Pb(II) and Cd(II) from soil by utilising sophorolipids of *Starmerella bombicola* CGMCC 1576 and reported about 95 and 52% of Cd and Pb removal percentage respectively by complexation mechanism in soil washing system. Secondly, as BSs can reduce the surface and interfacial tension of the medium, these get accumulated in the form of micelles on the solid/solution interface and bind the metal ions on themselves (Ayangbenro and Babalola, 2018). According to Tortora *et al.* (2016) the metal-BS complex or metal-micelle complex can be taken out from the system using micellar enhanced microfiltration (MEMF) or micellar enhanced ultrafiltration (MEUF). The efficiency of BSs depends on their size, class type, charge and structure that facilitates or determines their interaction with the sorbed metal on the soil (solid) surfaces (Wan *et al.*, 2017), also their translocation through soil pores on to the sorbed metal ions. Alternatively, the type of soil, its structure, contamination level and duration, pH, cation exchange capacity (CEC) and soil particle pore size also affects BS ability to remove metal ion from their surfaces or depth (Xue *et al.*, 2018; Pourfadakari *et al.*, 2019).

Surfactant/bio-surfactant modified low cost adsorbents (LCAs)

Chemically originated or biologically secreted surfactants are amphillic molecules having both hydrophilic and hydrophobic ends and are widely used in the HM remediation process where biological surfactants are preferred over chemically synthesised surfactants as the former have low toxicity, specificity, biodegradable nature, etc (Hailu *et al*., 2018). The natural materials such as zeolites and clays are known to be used as adsorbents in the HM removal process whose efficiency can be intensified by using acids or alkalies (Jimenez-Castaneda and Medina, 2017). In recent years, many studies have been conducted where these amphillic molecules when incorporated on such zeolites or clay materials, has increased the efficiency of the latter in the remediation process through ion exchange mechanism (Jimenez-Castaneda and medina, 2017; Li *et al*., 2007). Tran *et al.* (2018) explored the efficiency of cationic surfactant 'hexa-decyl-tri-methyl-ammonium' (HDTMA) modified organo-zeolite (Na-H-zeolite) in the removal of Pb, Cu, Ni and other organic pollutants. In a similar study, cationic surfactant 'hexa-decyl-tri-methyl-ammonium -bromide' C16 and zwitterionic surfactant 'hexa-decyl-di-methyl(3-sulphonatopropyl) ammonium' Z16 were applied on organo-montmorillonites for the removal of Cu(II) ions from the aqueous system (Ma *et al*., 2016).

Conclusion and recommendations

The application of non-conventional adsorbents and bacterial surfactants for the removal of heavy metal is gaining attention, owing to their easy availability, biodegradable nature and low toxicity. The agro-industrial wastes can be applied directly or in modified form for the treatment process and also can be used as substrates for the production of bio-surfactants making the remediation process more economical. The present chapter furnishes that this integrated approach can open up a novel aspect for remediation of heavy metal ions from the environment. Henceforth, more research is needed to be carried out to find new materials and novel bio-surfactants for environmental sustainability.

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