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REVIEW

# Algae as a green technology for heavy metals removal from various wastewater

El-Sayed Salama[1] · Hyun-Seog Roh[2] · Subhabrata Dev[3] · Moonis Ali Khan[4] · Reda A. I. Abou-Shanab[5,6] · Soon Woong Chang[7] · Byong-Hun Jeon[3]

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## Abstract

Urbanization, industrialization, and natural earth processes have potentially increased the contamination of heavy metals (HMs) in water bodies. These HMs can accumulate in human beings through the consumption of contaminated water and food chains. Various clean-up technologies have been applied to sequester HMs, especially conventional methods including electrolytic technologies, ion exchange, precipitation, chemical extraction, hydrolysis, polymer micro-encapsulation, and leaching. However, most of these approaches are expensive for large-scale projects and require tedious control and constant monitoring, along with low efficiency for effective HMs removal. Algae offer an alternative, sustainable, and environmentally friendly HMs remediation approach. This review presents a state-of-the-art technology for potential use of algae as a low-cost biosorbent for the removal of HMs from wastewater. The mechanisms of HMs removal, including biosorption and bioaccumulation along with physical and chemical characterization of the algae are highlighted. The influence of abiotic factors on HMs removal and changes in algal biocomponents (including, carbohydrate, lipid, and protein) are discussed. Recent progresses made in the development of HMs-tolerant algal strains and the direction of future research toward the development of sustainable technology for advanced wastewater treatment and biomass production are covered.

**Keywords** Phycoremediation · Heavy metals · Algae · Biosorption · Bioaccumulation · Abiotic factors

## Introduction

Surface and sub-surface water contamination caused by heavy metals (HMs) is of substantial global concern (Kobielska et al. 2018). HMs are released into the environment by natural processes including wind and floods, as well as through anthropogenic activities (Gupta et al. 2016). HMs present in the air and soil end up in water bodies due to precipitation and water run-off (Singare et al. 2010; Warmate et al. 2011). They are non-biodegradable and persistent, have a deleterious impact on both ecosystems and human health (Alqadami et al. 2018; Kwaansa-Ansah et al. 2019). Figure 1 schematically represents the toxic effects of HMs on different human organs. As the presence of HMs in aquatic environments may limit clean water availability for its intended usage (Dixit et al. 2015), therefore, stringent environmental regulations have been imposed to reduce HMs concentration in wastewater below permissible limits before discharging into natural water reservoirs. The maximum permissible limits of HMs reported by the United States Environmental

✉ Byong-Hun Jeon
bhjeon@hanyang.ac.kr

1 Department of Occupational and Environmental Health, School of Public Health, Lanzhou University, Lanzhou 730000, Gansu, People's Republic of China

2 Department of Environmental Engineering, Yonsei University, Wonju, Gangwon-do 220-710, South Korea

3 Department of Earth Resources and Environmental Engineering, Hanyang University, Seoul 04763, South Korea

4 Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia

5 Department of Environmental Biotechnology, City of Scientific Research and Technology Applications, New Borg El Arab, Alexandria 21934, Egypt

6 Biotechnology Institute, College of Biological Sciences, University of Minnesota, Saint Paul, MN 55108, USA

7 Department of Environmental Engineering, Kyonggi University, Suwon 16627, South Korea

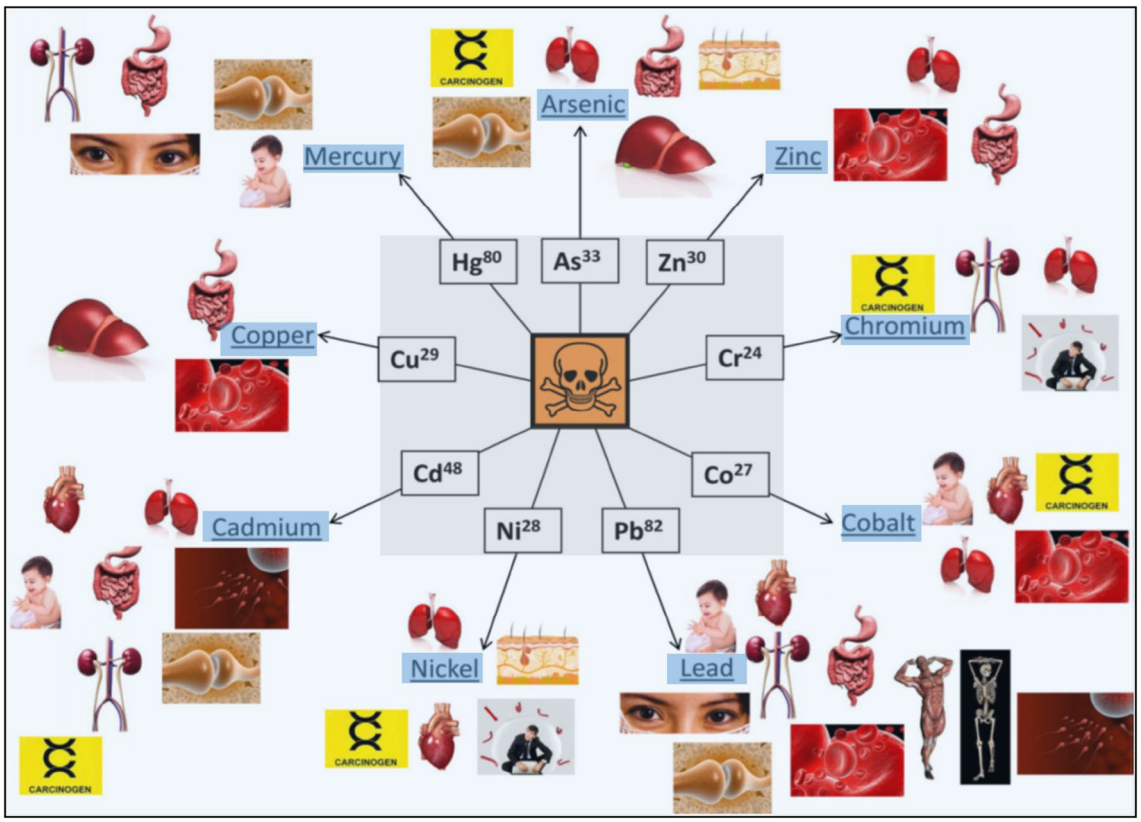


**Fig. 1** Schematic representation showing the organs and systems targeted in humans by HMs (de Namor et al. 2012)

Protection Agency (US-EPA) and the toxic effects of HMs on human health are presented in Table 1.

Various conventional techniques for HMs removal from polluted sites includes electrolytic technologies, ion exchange, precipitation, chemical extraction, hydrolysis, polymer micro-encapsulation, and leaching (Jais et al. 2017). However, the major concern is that most of these methods are ineffective, expensive when applied to large-scale projects, and require tedious control and constant monitoring. Table 2 covers the merits and demerits of conventional treatment processes. Therefore, biological treatment (bioremediation) is recommended as an alternative and eco-friendly approach for efficient removal of HMs from contaminated sites.

Bioremediation by algal species (Fig. 2), termed as "phycoremediation", has recently emerged as an appealing technique for HMs removal from wastewater (Ahmad 2016; Babu et al. 2013; Oyetibo et al. 2016; Poo et al. 2018). Phycoremediation has numerous advantages over other bioremediation processes including: (1) algal biomass can be applied in wastewater with higher metal concentration than for membrane processes (Brinza et al. 2007); (2) no need to synthesis algal biomass; (3) biomass can be regenerated and reused in several adsorption/desorption series; (4) high uptake capacity and efficiency of HMs removal (Ajayan et al. 2011); (5) no sludge or toxic chemical produced; (6) Macroalgal biomass does not essential to be immobilized; (7) algal biomass can be applied in discontinuous and continuous regimes; (8) by using dead biomass, no nutrient or oxygen supply needed; (9) appropriate for anaerobic and aerobic effluent treatment units; (10) algal biomass can be used all around year (Darda et al. 2019); and (11) cost effective (Kotrba 2011).

Therefore, considering the importance of algae as a promising agent for HMs removal, this review gives an overview on recent progresses made on HMs remediation by algae. The main mechanisms of HMs removal, including biosorption and bioaccumulation, are highlighted. The influence of several abiotic factors on HMs removal and changes in algal biocomponents are comprehensively discussed. Furthermore, recent progresses in the development of HMs-tolerant algal strains and directs future research toward the development of sustainable technology for wastewater treatment and biomass production are covered.

## Phycoremediation of HMs

Phycoremediation is defined as an application of algae in the treatment process of wastewater pollution (Jais et al. 2017). Algae are classified on the basis of their morphology, pigments, cell walls, stored food materials, reproductive

**Table 1** Toxic effects of heavy metals on human health (Dixit et al. 2015)

| Heavy metal | EPA regulatory limit (ppm) for drinking water contaminants | Hazardous effects to human health |
|---|---|---|
| Pb | 15.00 | • Excessive exposure in children causes impaired development and reduced intelligence<br>• Short-term memory loss<br>• Learning disabilities and coordination problems<br>• Risk of cardiovascular disease |
| Se | 50.00 | • Dietary exposure of ~ 300 µg $day^{-1}$ affects endocrine function<br>• Impairment of natural killer cells activity<br>• Hepatotoxicity and gastrointestinal disturbaces |
| Hg | 2.00 | • Memory loss<br>• Hair loss<br>• Vision disturbance<br>• Lung and kidney failure<br>• Autoimmune diseases |
| Ba | 2.00 | • Cardiac arrhythmias<br>• Respiratory failure<br>• Gastrointestinal dysfunction<br>• Elevated blood pressure |
| Cu | 1.30 | • Brain and kidney damage<br>• Elevated levels result in liver cirrhosis<br>• Chronic anemia<br>• Stomach and intestinal irritation |
| Zn | 0.50 | • Dizziness and fatigue |
| Ni | 0.20 | • Allergic skin diseases<br>• Cancer of the lungs, nose, sinuses, or throat through continuous inhalation<br>• Immunotoxic, neurotoxic, genotoxic |
| Cd | 5.00 | • Carcinogenic<br>• Endocrine disruptor<br>• Lung damage and fragile bones<br>• Affects calcium regulation in biological systems |
| Cr | 0.10 | • Hair loss |
| Ag | 0.10 | • Exposure may cause skin and other body tissues to turn gray or blue-gray<br>• Breathing problems<br>• Lung and throat irritation and stomach pain |
| As | 0.01 | • Affects essential cellular processes such as oxidative phosphorylation and ATP synthesis |

*US EPA* United States Environmental Protection Agency

structures, and life history patterns into seven major groups: *Rhodophyta*, *Chlorophyta*, *Charophyta*, *Chrysophyta*, *Euglenophyta*, *Pyrrhophyta*, and *Phaeophyta* (Hallmann 2015; Namdeti and Pulipati 2014; Wang and Chen 2009). Various HMs, such as $Mn^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Mo^{2+}$, $Fe^{2+}$, and $Zn^{2+}$, are essential to algal growth and are known as 'trace elements' that are desirable as micronutrients. In contrast, other HMs, including $Sn^{2+}$, $Au^{3+}$, $Cd^{2+}$, $Pb^{2+}$, $Sr^{2+}$, $Ti^{3+}$, and $Hg^{2+}$, have no essential biological function and are toxic to algae (Jais et al. 2017). Detailed studies of the physiochemical composition of algal cells have helped in revealing the usefulness of algae in environmental pollution control, especially in the area of HMs removal from domestic and industrial wastewaters. Some algae have shown exceptional tolerance and survival in water polluted with relatively high HMs concentration (Kotrba 2011).

Besides living cells (Fig. 3a, b), the dead algal cells can also remove HMs from contaminated water as both can perform biosorption of HMs present in their surrounding environment (Fig. 3c). However, the efficiency of living algae cells during wastewater treatment is higher than that of dead biomass, as they can remove and retain a greater quantity of metals using both biosorption and bioaccumulation mechanisms for a longer time period. The HMs removal efficiencies of various algal species in various wastewater sources (e.g., municipal, petrochemical, electroplating, and dairy) are shown in Table 3. For example, *Spirulina* sp. removed 91 and 98% of $Cu^{2+}$ and $Ca^{2+}$ after cultivation in municipal wastewater, respectively (Al-Homaidan et al. 2015; Anastopoulos and Kyzas 2015). When grown in municipal wastewater, the removal efficiency of *Chlorella minutissima* was 62, 84, 74, and 84% for $Zn^{2+}$, $Mn^{2+}$, $Cd^{2+}$, and $Cu^{2+}$, respectively (Yang et al. 2015). After cultivation in oil sands tailings ponds, *Cladophora fracta* removed 99% of $Cu^{2+}$ and 85% of $Zn^{2+}$ (Mahdavi et al. 2012). After grown in acid mine drainages, the removal efficiency of

**Table 2** Heavy metal remediation technologies: disadvantages and advantages (Alfarra et al. 2014; Parmar and Thakur 2013)

| Method | Disadvantages | Advantages |
|---|---|---|
| Chemical precipitation | • Difficult separation<br>• pH dependent<br>• Resulting sludge<br>• Adverse influence by completing agent<br>• Chemicals needed | • Simple and inexpensive |
| Ion exchange | • High operational cost<br>• Sensitive to particles<br>• Prone to fouling of resin by precipitates and organics<br>• Oxidation of resin by chemicals | • No sludge generation<br>• Pure effluent metal recovery possible |
| Membrane | • Metallic fouling<br>• No selectivity to alkaline metals<br>• High-pressure<br>• Partial life of membrane<br>• Costly | • Pure effluent |
| Flocculation and coagulation | • Depend on basin design<br>• Chemicals required (electrolytes) | • Generate very fine particles of precipitates |
| Flotation | • Less selective for HMs | • Inexpensive |
| Electrodialysis | • Large electrode surface area is essential<br>• Time-consuming<br>• Costly<br>• Membrane fouling | • Metal-selective |

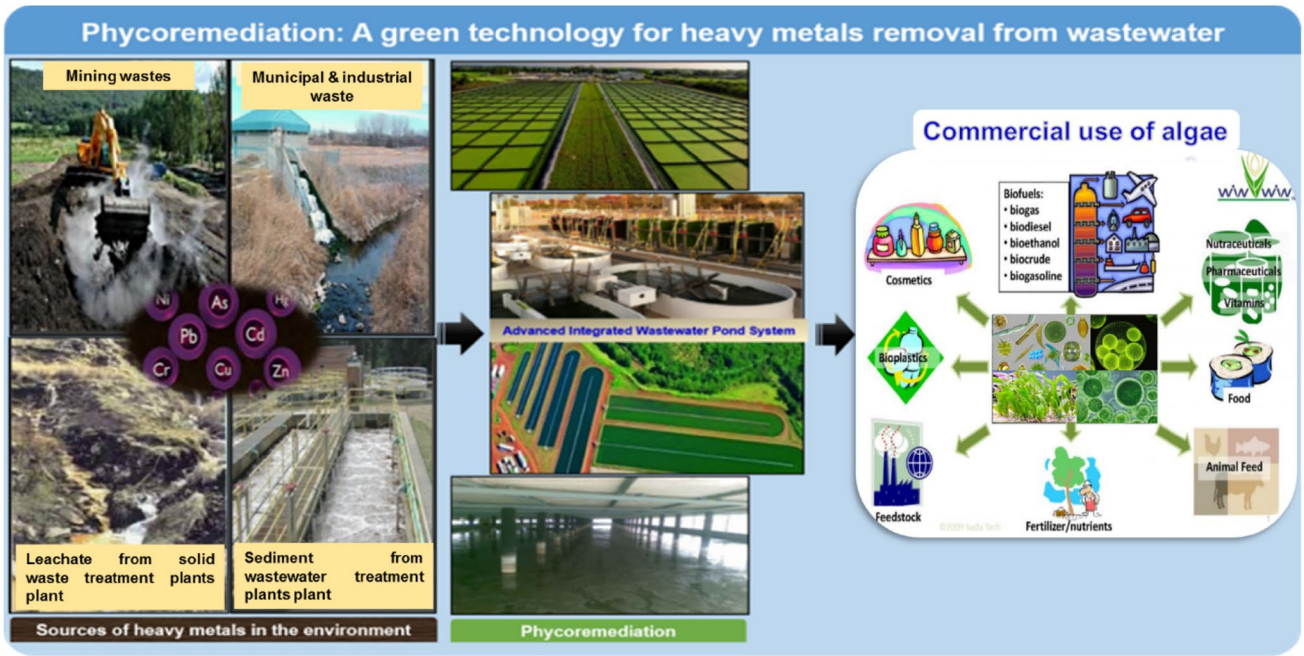


**Fig. 2** Application of algae for removal of heavy metals from wastewater and biomass utilization

*Oedogonium* sp. was 46, 34, 48, and 50% for $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, and $Co^{2+}$, respectively (Bakatula et al. 2014). In Vasant Kunj, New Delhi, India, arsenic (As) was completely removed from drinking water by the filamentous green alga *Cladophora* (Jasrotia et al. 2014). *Chlorella* sp., *Scenedesmus* sp., and *Chlamydomonas* sp. have shown to be effective in removing HMs, some toxic organic compounds, and secondary pollutants from wastewaters with a wide range of initial pollutant concentrations (Gao et al. 2016; Matamoros et al. 2015; Yang et al. 2016).

Algal biomass could be considered as an alternate to conventional adsorbent materials (including microbial,

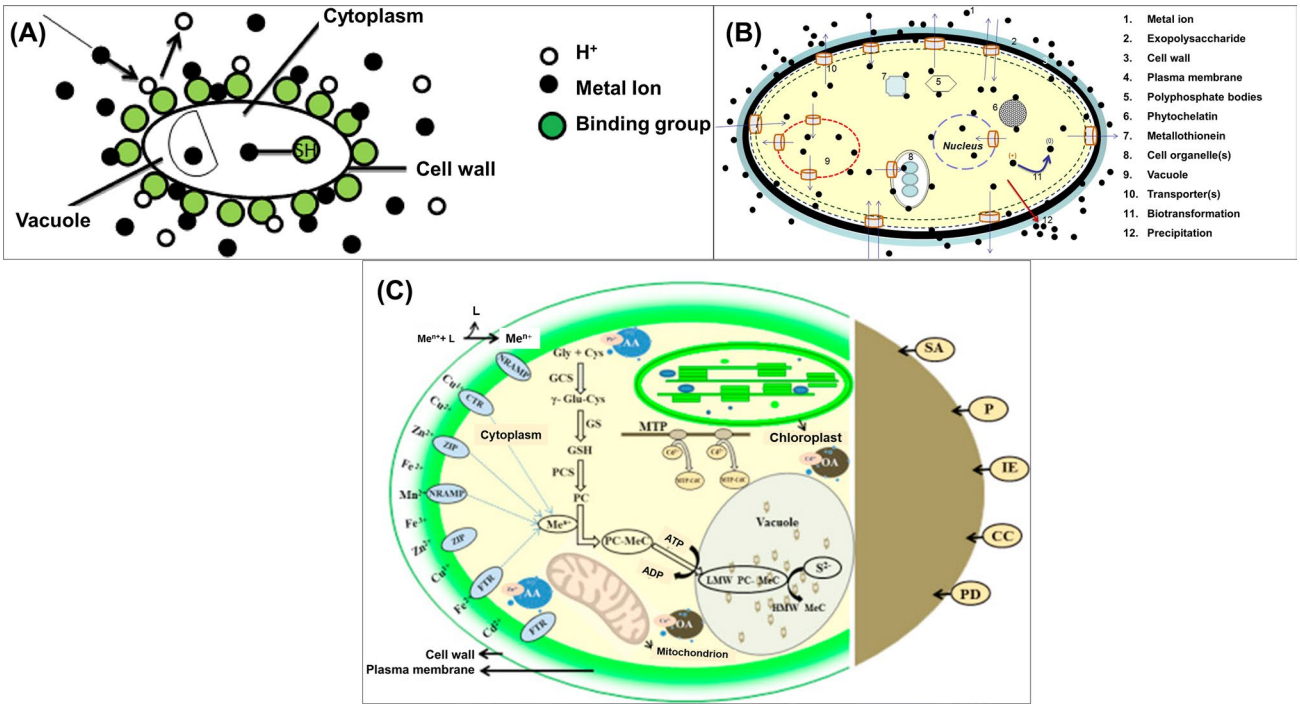


**Fig. 3** Various binding groups ($COO^-$, $OH^-$, $PO_4^{3-}$, $NO_3^-$, $SH^-$, $RNH_2^-$, $RO^-$, and $RS^-$) stimulate metal ion biosorption (**a**). A schematic representation of surface binding, uptake, and intracellular accumulation of metal ions by a living algal cell. A variety of transporters is involved in uptake of metal ions, and the cell has numerous intracellular sites for binding and sequestration of metal ions (**b**). A schematic representation of some mechanisms of HMs sequestration, translocation, and uptake in living (left) and non-living (right, brown-shaded) algae (**c**) (Kumar et al. 2015, 2016; Zeraatkar et al. 2016)

agricultural waste or other type of biomasses) for the treatment of HMs due to: (1) algae can be grown in a wide range of environmental conditions (Abou-Shanab et al. 2011); (2) they show high growth rates because of short cell cycle time; (3) they require low nutrient concentrations compared to other biomass organisms; (4) they do not need agricultural land for cultivation; (5) due to lower water requirements, algae cultivation can be achieved in wastewater (Salama et al. 2017); and (6) they can be further used for other applications such as biofuel generation (Mantzorou et al. 2018).

## Mechanisms of HMs phycoremediation

Several studies have reported the potential of phytoplankton to sequester HMs from aqueous media (Jan and Parray 2016; Lahiri et al. 2017). Microalgae remove HM ions from wastewater through two mechanisms: biosorption and bioaccumulation (Table 4). Biosorption is an independent metabolic process that occurs in both live and dead cells (Fig. 3). In this process, HM ions attached to functional groups on the cell surface as a result of ion exchange, complexation, chelation, and microprecipitation (Kumar et al. 2015; Park et al. 2016). Studies suggest that the components of algal cell walls, such as alginate and fucoidan, which have key functional groups, are chiefly responsible for biosorption of HM ions (Anastopoulos and Kyzas 2015; Zeraatkar et al. 2016). Through ion exchange, the HM ions in wastewater surrounding the algae are exchanged with elemental ions held on the cell surface, such as $Ca^{2+}$, $Na^+$, and $K^+$. The viability of this process depends on important factors such as metal selectivity and regeneration potential. Selectivity in biosorption is generally low because HM ions bind to the cell surface through physicochemical interactions. However, selectivity can be increased through chemical modification of the biomass, such as cross-linking with epichlorohydrin, or oxidation by potassium permanganate (Luo et al. 2006). Figures 3 and 4 present the biosorption and bioaccumulation processes for HM ions removal.

## Biosorption

Biosorption is a physiochemical property of biological material that results in the removal of pollutants, mostly HMs, from wastewater by either ionic or covalent bonding (He and Chen 2014; Zeraatkar et al. 2016). Various binding groups, such as $COO^-$, $SH^-$, $OH^-$, $RNH_2^-$, $RS^-$, and $RO^-$, promote metal ion biosorption (Fig. 3a, b). These binding groups are present at the cell surface and in the cytoplasm, especially inside vacuoles. Studies have shown that algal cell walls carry a net negative charge due

**Table 3** Algae removal efficiency of metal ions from various wastewaters

| Microalgae strain | Media | Reactor type | Metal | Removal efficiency (%) | Mechanism | References |
|---|---|---|---|---|---|---|
| *Spirulina platensis* | Wastewater | Batch | $Cu^{2+}$ | 91 | Biosorption | Anastopoulos and Kyzas (2015) |
| *Pterocladia capillacea* | Wastewater | Batch | $Cr^{3+}$ | 20–100 | Sorption | El Nemr et al. (2015) |
| *Chlamydomonas reinhardtii* | – | Batch | La | 30–100 | Adsorption/desorption | Birungi and Chirwa (2014) |
| *Scenedesmus acuminutus* | | | | 50–90 | | |
| *Chloroidium saccharophilum* | | | | 35–80 | | |
| *Spirulina platensis* | Wastewater | Batch | $Ca^{2+}$ | 98 | Adsorption | Al-Homaidan et al. (2015) |
| *Chlorella* sp. | Wastewater | Batch | $Ca^{2+}$ | 56 | Biosorption | Raikova et al. (2016) |
| *Chlorella* sp. | | | $Mg^{2+}$ | 56 | | |
| *Scenedesmus* sp. | | | $Ca^{2+}$ | 59 | | |
| *Scenedesmus* sp. | | | $Mg^{2+}$ | 29 | | |
| *Spirulina maxima* | – | In situ set up | $Cr^{3+}$ | 77 | Biosorption | Singh et al. (2016) |
| *Chlorella minutissima* | Municipal wastewater | Batch | $Zn^{2+}$ | 62 | Adsorption | Yang et al. (2015) |
| | | | $Mn^{2+}$ | 84 | | |
| | | | $Cd^{2+}$ | 74 | | |
| | | | $Cu^{2+}$ | 84 | | |
| Mixed culture (*Eichhornia crassipes*, *Lemna minor*, and *Spirodela polyrhiza*) | – | In situ set up | As and other HMs | 0.04 | Detoxification | Singh et al. (2016) |
| *Cystoseira stricta* | Aqueous solutions | Batch | $Pb^{2+}$ | 10 | Biosorption | Iddou et al. (2011) |
| *Chitosan algal biomass* | Microbeads | Batch | $Cd^{2+}$ | 37 | Adsorbent | Sargın et al. (2016) |
| | | | $Cr^{3+}$ | 68 | | |
| | | | $Cu^{2+}$ | 48 | | |
| | | | $Ni^{2+}$ | 27 | | |
| | | | $Zn^{2+}$ | 49 | | |
| *Cladophora fracta* | Oil sands tailings pond water | Batch | $Cu^{2+}$ | 99 | Biosorption | Mahdavi et al. (2012) |
| | | | $Zn^{2+}$ | 85 | | |
| – | Aqueous media | Batch and continuous | $Cd^{2+}$ | 78 | Biosorption | Bulgariu and Bulgariu (2016) |

**Table 3** (continued)

| Microalgae strain | Media | Reactor type | Metal | Removal efficiency (%) | Mechanism | References |
|---|---|---|---|---|---|---|
| *Spirulina platensis* | Aqueous solutions | Batch | $Cu^{2+}$ | 91 | Biosorption | Anastopoulos and Kyzas (2015) |
| *Chlorella miniata* | Aqueous solutions | | $Cr^{3+}$ | 85 | | |
| *Scenedesmus quadricauda* | | | $Cr^{6+}$ | 60 | | |
| *Dunaliela Algae* | | | $Cd^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Cr^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ | 74–95 | | |
| *Ulva lactuca* | | | $Hg^{2+}$ | 60–86 | | |
| *Jania rubens* | | | $Hg^{2+}$ | 54–71 | | |
| *Sphaerococcus coronopifolius* | | | $Hg^{2+}$ | 70–90 | | |
| *Ulva lactuca* | | | $Cr^{6+}$ | 96 | | |
| *Azolla filiculoides* | | | Cr6 | 83 | | |
| *Sargassu myriocystum* | | | $Pb^{2+}$ | 87 | | |
| *Caulerpa fastigiata* | | | $Pb^{2+}$ | 70–82 | | |
| *Osmundea pinnatifida* | | | $Cd^{2+}$ | 75 | | |
| *Osmundea pinnatifida* | | | $Cu^{2+}$ | 70 | | |
| *Cystoseira indica* | | | $Co^{2+}$ and $Cu^{2+}$ | 90 | | |
| Mixed culture (*Ascophyllum nodosum, Fucus spiralis, Laminaria hyperborea*, and *Pelvetia canaliculata*) | Petrochemical wastewater | Batch and continuous | $Zn^{2+}$ | 93 | Molar fraction Ion exchange | Cechinel et al. (2016) |
| | | | $Ni^{2+}$ | 94 | | |
| | | | $Cu^{2+}$ | 94 | | |
| *Chlorella* sp. | Wastewater | Batch | $Ca^{2+}$ | 56 | Sorption | Wang et al. (2016b) |
| *Scenedesmus* sp. | | | $Ca^{2+}$ | 59 | | |
| *Chlorella* sp. | | | $Mg^{2+}$ | 56 | | |
| *Scenedesmus* sp. | | | $Mg^{2+}$ | 29 | | |
| *Chlorella* sp. | Bold basel media | Batch | $Pb^{2+}$ | – | Active and passive uptake mechanisms | Dao and Beardall (2016) |
| *Scenedesmus* sp. | | | $Pb^{2+}$ | – | | |
| *Cladophora* sp. | Drinking water | Batch | As | 100 | Biosorption | Jasrotia et al. (2014) |
| *Oedogonium* sp. | Acid mine drainage | Batch | $Cu^{2+}$ | 46 | Biosorption | Bakatula et al. (2014) |
| | | | $Ni^{2+}$ | 34 | | |
| | | | $Zn^{2+}$ | 48 | | |
| | | | $Co^{2+}$ | 50 | | |
| | | | Fe | 37 | | |
| | | | Hg | 16 | | |
| | | | U | 34 | | |
| | | | C | 39 | | |
| *Laminaria japonica gel* | Wastewater | Batch & continuous | Mo and Re | 60–100 | Sorption | Lou et al. (2015) |

to the presence of $COO^-$, $PO_4^{3-}$, and other groups used for bonding metals through ion exchange. Some algal species, including *Ditylum brightwellii*, secrete a special substance called Cu ligands (Rijstenbil and Gerringa 2002). The carboxyl functional group ($COO^-$) is the most abundant acidic functional group in the cell walls of brown algae. Excretion and exclusion of metal from the cell, as well as the production of proteins like proline and other

**Table 4** Comparison of biosorption and bioaccumulation processes (Zabochnicka-Świątek and Krzywonos 2014)

| Characteristics | Biosorption | Bioaccumulation |
|---|---|---|
| Removal rate | Most mechanisms take place at a fast rate | Slower rate than biosorption |
| Selectivity | Poor, can be increased by modification/biomass transformation | Better than biosorption |
| Metal recovery | HM recovery is possible with adequate eluent | Even if possible, biomass cannot be used for other purposes |
| pH | Strongly affects the sorption capacity of HMs; however, the process can occur within a wide pH range | Significant pH change can strongly affect living cells |
| Regeneration and reuse | Biosorbents can be regenerated and reused in many cycles | Partial reuse because of intercellular accumulation |
| Energy required | Usually low | Energy needed for cell growth |
| Cost | Usually low; biomass can be obtained from industrial waste, and cost is mostly associated with transportation and production of biosorbent | Process occurs in the presence of living cells that have to be sustained |

binding compounds like metallothioneins (MTs) and glutathione (GSH), are among the mechanisms employed by algae to prevent metal-induced damage (Aude-Garcia et al. 2016). Differences in cell wall components among various algal species result in different functional groups. The metal uptake of biosorbent and the matrix system was quantitatively evaluated using Pb, Cd, Ni, and Zn and corresponded well with the Langmuir isotherm model (Aziz et al. 2016). The selectivity of HMs uptake depends on the encapsulation of microalgae and its cellulose derivatives (Wang et al. 2016a). Desorption of the adsorbed HMs can be achieved through a reduction in the suspension pH. Therefore, a reversible loading/unloading of the adsorbed HMs, using HCl or citric acid for the desorption process, is possible.

Metal biosorption experiments have been carried out with freshwater green microalgae (e.g., *Chlorella* sp., *Scenedesmus* sp., and *Chlamydomonas* sp.), brown algae (e.g., *Fucus vesiculosus* and *Laminaria japonica*), and blue-green algae (e.g., *Microcystis aeruginosa* and *Oscillatoria* sp.) (Khan et al. 2017). Several HMs removal technologies, for example, high rate algal ponds (HRAP) and algal turf scrubbers (ATS), have been supported for practical applications around the globe. However, these technologies are still insufficient for large-scale application. As an innovative clean-up technology, phycoremediation depends mainly on the biosorption and bioaccumulation abilities of algae, with biosorption dominating the bioremediation process (Furey et al. 2016).

Algae are efficient and cost-effective biosorbents due to their low nutrient requirements. Based on statistical analysis of the potentiality of algae for biosorption, the biosorption efficiency of algae has been reported as approximately 15.3–84.6% higher than other microbial biosorbents (e.g., bacteria and fungi) (Anastopoulos and Kyzas 2015; Kanchana et al. 2014; Sweetly 2014).

## Bioaccumulation and detoxification of heavy metals in algae

Through bioaccumulation, HM ions are transported across living cell membranes in various ways (e.g., active and passive transport systems) and accumulated within cells (Figs. 3 and 4a). HMs accumulation inside the cell causes inhibition of photosynthesis activity and thus reduce the algal growth, irreversible increase in plasma-lemma permeability leading to the loss of cell solutes, disruption of membrane integrity owing to deterioration of protein structure, enzyme inhibition due to displacement of essential metal ions, abnormal morphological development, and loss of flagella in certain algae (Fig. 4b). Intracellular and extracellular metal binding approaches (such as ion exchanges, chelation, physical adsorption, and complexation) have been implemented by algae to overcome HMs toxicity (Priyadarshini and Priyadarshini 2019). These mechanisms are effective as they alter the toxic metal into non-toxic forms (Mantzorou et al. 2018).

Metal detoxification by algae is achieved through several approaches including binding to specific intracellular organelle or transport to specific cellular components (such as polyphosphate bodies/vacuoles), flushing out into the solution by efflux pump, and synthesis of phytochelatins or class III metallothioneins (Perales-Vela et al. 2006). A detoxification process can reduce the toxicity of HM ions on living cells through precipitation in a carbonate, phosphate, or sulfide forms (Juang and Chang 2016). *Cladophora glomerata*, a green alga, was able to remove Pb, Cd, Ni, Cr, and V at 7.9, 0.1, 15.6, 1.7, and 37.7 mg $kg^{-1}$, respectively, from a refinery sewage lagoon (Chmielewská and Medved 2001). *Fucus vesiculosus*, a macroalga, showed high capacity for HMs accumulation from contaminated saltwater, removing

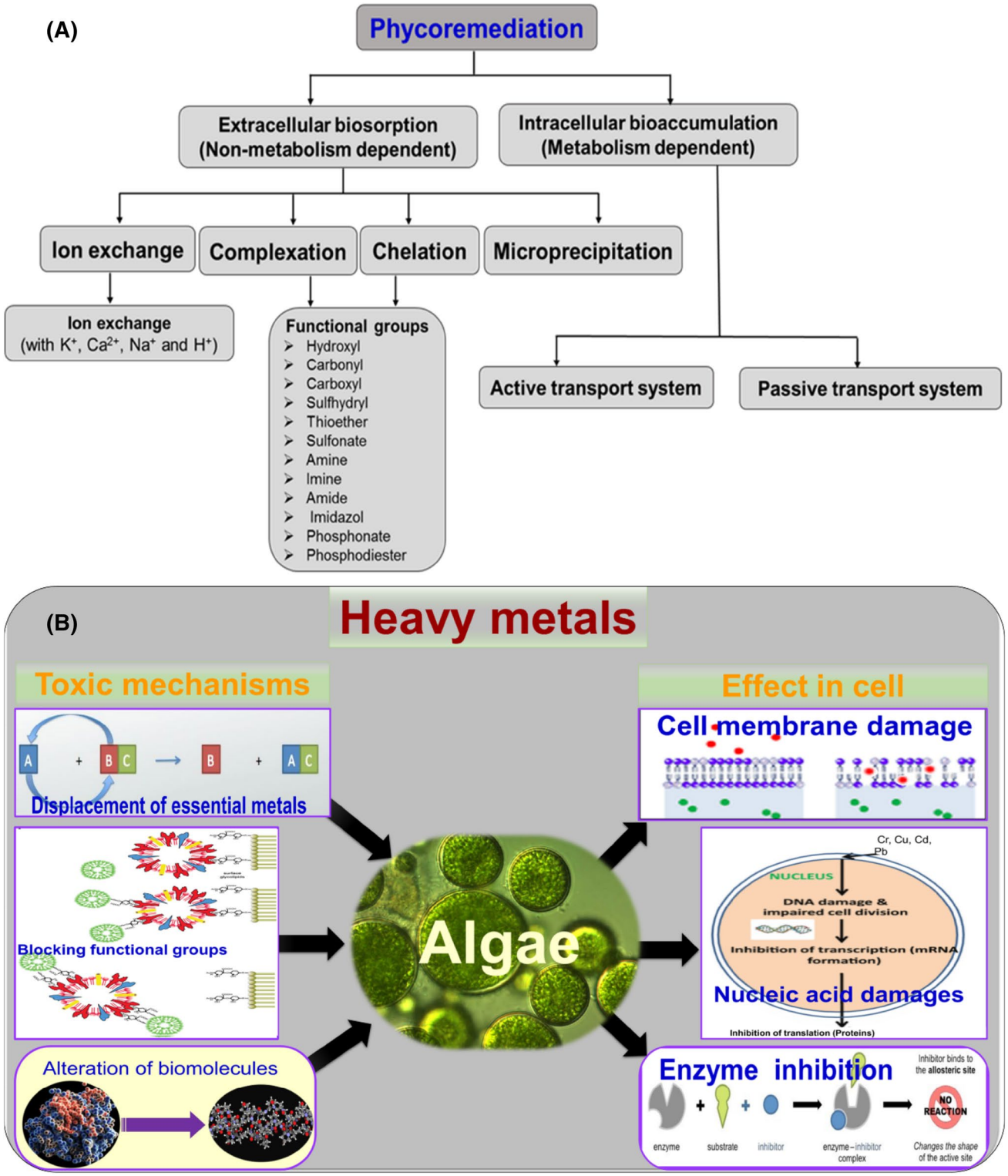


**Fig. 4** Phycoremediation approaches for HMs removal (**a**). The toxic mechanisms and effects on algal cell by HMs (**b**)

65, 95, and 76% of Pb, Hg, and Cd, respectively. Bioconcentration factors for Pb, Hg, and Cd ranged from 600 to 2300, with all metal removed from the solution accumulated into the biomass (Henriques et al. 2017).

## Abiotic factors influencing HM remediation by algae

### Media pH

Availability of the metal-binding groups on algae invariably depends on pH of the media. These groups can maintain negatively charged surface under acidic conditions. However, extreme pH (< 2) was reported for lowering the metal biosorption by microalgae. High concentrations of $H^+$ ions decrease metal biosorption by preventing them from binding to ligands on the cell surface (Volesky 2007; Zeraatkar et al. 2016). Various binding groups and ligand atoms in algae biomolecules are listed in Table 5. According to the $pK_a$ of functional groups, carboxyl groups, sulfonate, phosphate, and phosphodiester are the largest contributors in metals biosorption. Different algae exhibit different capacity for metal ions biosorption because of the relative abundance of each functional groups for different algal strains (Priyadarshini and Priyadarshini 2019).

Optimization of the suspension pH is vital for maximum biosorption capacity and efficiency. Therefore, efforts have been made to determine the optimum pH values for enhancement in metal ions removal by algae (Sheng et al. 2005). Biosorption of $Cs^+$ by *Padina australis* was optimal at pH 4 (Jalali-Rad et al. 2004). $Cu^{2+}$ biosorption was strongly governed by solution pH. Lower $Cu^{2+}$ biosorption was observed at acidic pH (~ 2), gradual increased at higher suspension pH. The sharpest increase was observed between pH 3 and 4 (Yu and Kaewsarn 1999). Biosorption of $Pb^{2+}$ by *Durvillaea potatorum* was optimal at pH 5 (Jalali-Rad et al. 2004). The biosorption of some metal ions such as $Cu^{2+}$ and $Pb^{2+}$ might increase using living algal cells, because of consequent increase in suspension pH due to photosynthetic activity (Raeesossadati et al. 2014). Thus, injection of $CO_2$ can be used to control the acidity of the culture medium (Zeraatkar et al. 2016).

For efficient HMs removal by an algal biosorbent, the ratio of free metal ions $[M^{n+}]$ to total metal concentration $[M]_T$ should remain high (Babarinde and Onyiaocha 2016). The ratio of $[M^{n+}]$ to $[M]_T$ in a solution can be determined by the free ligand concentration and stability constant (β). $[M^{n+}]/[M]_T$ is often low for $Fe^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Pb^{2+}$, and $Hg^{2+}$ at circumneutral pH due to relatively low solubility and frequent surface precipitation on microalgae has been also observed (Abou-Shanab et al. 2013; Babarinde and Onyiaocha 2016). Most of the relevant studies have disregarded this important aspect during screening of algal species for biosorption of metals from metal solutions or industrial effluents.

### Ionic strength

The ionic strength influence is caused by the competition between HMs and $Na^+$ for electrostatic binding to the algal biomass, which carries a negative charge. Most of the negative charges in the algal biomass balanced at the high ionic strength. However, at lower ionic strength, the electrostatic attraction leads to higher intraparticle protons concentration than the bulk proton concentration (Andrade et al. 2005; Schiewer 1999). Characterizations of *Ulva fascia* (green alga), *Sargassum hemiphyllum*, *Petalonia fascia*, and *Colpomenia sinuosa* (brown seaweeds) were performed in terms of their charge density, binding sites, and intrinsic proton binding constant ($pK_a$). The number of identified binding

**Table 5** The major functional groups and classes of organic compounds in algae known to be involved in the biosorption process (Volesky 2007; Zeraatkar et al. 2016)

| Binding group | Structural formula | $pK_a$ | Ligand atom | Occurrence in selected biomolecules |
|---|---|---|---|---|
| Hydroxyl | –OH | 9.5–13 | O | Polysaccharides, uronic acids, sulfated, and amino acids |
| Carbonyl (ketone) | C=O< | – | O | Peptide bond |
| Carboxyl | –C=O–OH | 1.7–4.7 | O | Uronic acids and amino acids |
| Sulfhydryl (thiol) | –SH | 8.3–10.8 | S | Amino acids |
| Sulfonate | O–S=O | 1.3 | O | Sulfated |
| Thioether | S< | – | S | Amino acids |
| Amine | $=NH_2$ | 8–11 | N | Chitosan and amino acids |
| Secondary amine | >NH | 13 | N | Peptidoglycan and peptide bond |
| Amide | $–C=ONH_2$ | – | N | Amino acids |
| Imine | =NH | 11.6–12.6 | N | Amino acids |
| Imidazole | –C–N–H >CH H–C–N | 6.0 | N | Amino acids |
| Phosphonate | OH–P=O–OH | 0.9–2.1 | O | Phospholipids |
| | | 6.1–6.8 | O | Phospholipids |
| Phosphodiester | >P=O–OH | 1.5 | O | Phospholipids |

sites were highest on *Petalonia* and *Sargassum* and lowest on *Colpomenia* and *Ulva* (Schiewer and Wong 2000). Due to the large number of binding sites, *Sargassum* and *Petalonia* were most effective for biosorption applications. A decrease in proton binding with increased ionic strength and pH was described using the Donnan model, in conjunction with an ion exchange biosorption isotherm. Electrostatic attraction between protons and negatively charged carboxyl sites results in intraparticle proton concentrations that are higher than the bulk proton concentration, resulting in proton release from intraparticle space into the bulk solution (Ungureanu et al. 2016). A $pK_a$ value of 3.0 was used for all algae, and it was assumed that the cation binding volume was proportional to the number of binding sites. The $Cu^{2+}$ binding constants decreased in the following order: *Sargassum* > *Petalonia* > *Colpomenia* > *Ulva*. The intrinsic binding constant for $Cu^{2+}$ was 30-90 times higher than that for $Ni^{2+}$. Covalent binding was more important for $Cu^{2+}$ than for $Ni^{2+}$, which was bound predominantly by electrostatic attraction (Kleinübing et al. 2013). Virtually no covalent metal binding took place in *Ulva*, possibly, because green algae, which lack alginate, do not offer carboxyl groups spaced at suitable distances for metal ions to bridge between two binding sites. Brown algae are more suited for biosorption applications than green algae because of their higher metal binding capacity and affinity (Davis et al. 2003).

### Temperature

The biosorption efficiency of algal species for each metal ions is effected by temperature (Chairat and Bremner 2016; Gupta et al. 2010). Although the constants for metal–ligand complex formation are primarily a function of temperature, some studies have claimed that a potential increase in metal ions biosorption is due to an increases in algal culture temperatures, without considering changes to formation constants (Khan et al. 2012; Yi et al. 2016). The possible reasons for an increase in biosorption with an increase in temperature are: (a) increase in the number of active sites involved in metal ions uptake; (b) increase in the tendency of active sites to absorb metal ions; (c) a reduction in mass transfer resistance in the diffusion layer due to a reduction of the diffusion boundary layer thickness around the biosorbent groups; or (d) a change to the complex formation constant with temperature (Bayes et al. 2012; Zhu and Wachs 2016). However, other studies have suggested that for some algae, the metal ions uptake was exothermic, so by lowering the temperature, uptake capacity increases. Several studies reported temperature-linked changes in metal ions uptake by living algal cells, while others also showed that temperature has no significant influence on metal ions uptake by dead algal cells (Balarak et al. 2016). These seemingly incompatible results may be resolved by noting that optimum temperatures are usually a narrow range for active biological reactions in living cells. A biomass of *Chlorella vulgaris* achieved maximum biosorption of $Cd^{2+}$ and $Ni^{2+}$ at 20 and 45 °C, respectively (Aksu 2001). Temperature also influences metal ions biosorption on non-living algal biomass, as the biosorption equilibrium is determined by the exothermic or endothermic nature of the process (Al-Homaidan et al. 2014). A number of studies have examined the effects of temperature on biosorption isotherms, metal uptake, and biosorption thermodynamics parameters (Pokethitiyook and Poolpak 2016). Due to biosorption and the involvement of enzymes in ion transfer, increased temperature might have a greater impact on the biosorption capacity of living algae compared to non-living algae (Goher et al. 2016). In the available literature reported on temperature effect, it is difficult to develop a relationship between temperature and metal ions uptake. However, different algal strains behave differently to uptake metals ions at varied temperatures (Chang 2019; Furuhashi et al. 2019; Mantzorou et al. 2018; Vilar et al. 2005).

### Effect of counter ions

The presence or absence of other ions in the medium along with nutrient level, growth rate, and illumination greatly influence metal ions biosorption by living algae. The uptake of $Cd^{2+}$ by *Aphanocapsa* increased with increased $NO_3^-$ concentration in the culture medium (Quan et al. 2016). The growth phase of the algal culture also influences metal ions biosorption. Biosorption of $Ni^{2+}$ on the surface of *C. vulgaris* was higher for cultures in the stationary and decline phases than in the exponential phase, this might be a result of higher exposure of the metal binding sites or from creation of additional sites on the cell surface during these phases. Metal ions biosorption characteristics of the biomass may be influenced by growth conditions as it effects the cell surface composition which is a key player in metal ions biosorption (Wu et al. 2016).

### Impact of contact time

HM ions biosorption is highly dependent on contact time. The kinetics of HM ions biosorption on algae cell surfaces in previous studies report that the biosorption mechanism is specific to various algal strains (Sooksawat et al. 2016; Zhang et al. 2016). Biosorption occurs in two stages (Chang 2019; Gupta et al. 2017). First, for algal biomass, metal ions were passively adsorbed to cell membranes, and biosorption of metal ions occurs rapidly within the first minute. Second, for live algae, active biosorption occurs as the algal cell slowly uptakes the HM ions. The uptake of uranium (U) by biomass of non-living *C. vulgaris* during the first 5 min was more than 90% (Sooksawat et al. 2016; Vogel et al. 2010).

Biomass of *Chlamydomunas reinhardtii* microalgae rapidly adsorbed free ions of $Hg^{2+}$, $Cd^{2+}$, and $Pb^{2+}$, with biosorption equilibrium achieved in 60 min (Nowicka et al. 2016; Tüzün et al. 2005). This demonstrates that biosorption of HM ions is a passive process that occurs relatively rapidly even when algal cells are non-living. In living algae, contact time has a greater effect on biosorption capacity.

### Phytohormones

Earlier studies have shown that exogenous application of phytohormones can improve protection against HMs toxicity. Acting as chemical messengers with highly complex regulation, these molecules allow algae to retain growth plasticity during the development. Additionally, phytohormones are collectively the main means by which plants respond to abiotic and biotic stresses (Asgher et al. 2016; Krantev et al. 2008; Masood et al. 2016). Phytohormones (i.e., auxins, cytokinins, gibberellin, and polyamine) alleviate the effects of HMs stress on growth and prevent degradation of photosynthetic pigments, monosaccharides, and proteins. These compounds prompt a mechanism of plant stress tolerance, which is associated with the blockage of HMs entry into the cell and the activation of antioxidant defense responses that reduce oxidative damage stimulated by HMs. Piotrowska-Niczyporuk et al. (2012) clearly indicated the ameliorative influence of auxins, cytokinins, gibberellin, and polyamine on algal resistance to HMs and growth improvement. Jasmonic acid acted as a stressor that stimulated metal biosorption, which led to inhibition of algal growth and metabolite oxidative degradation. These results suggest that phytohormones plays a vital role in the ability of *C. vulgaris* to grow and develop adaptively in aquatic ecosystems contaminated with HMs (Piotrowska-Niczyporuk et al. 2012). The interactions among HMs, phytohormones, and polyamine are unclear and require further study. Figure 5 shows a schematic representation of phytohormones reaction, including abscisic acid, auxin, brassinosteroids, and ethylene, under HMs exposure.

### Effect of HMs on the bio-components of algae

Lipid production combined with HMs removal is a cost-effective and environmentally friendly approach for algae

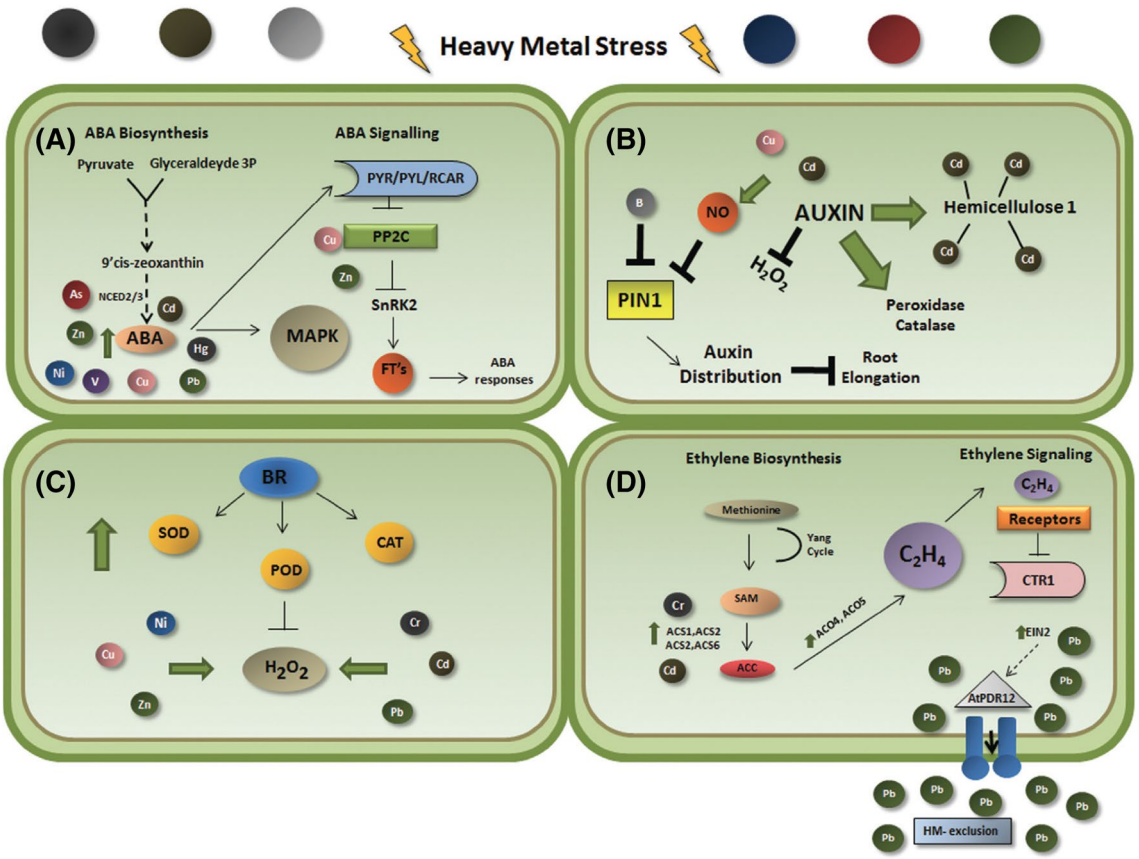


**Fig. 5** A schematic illustration showing reactions of some phytohormones under HMs exposure: abscisic acid (**a**), auxin (**b**), brassinosteroids (**c**), and ethylene (**d**) (Bücker-Neto et al. 2017)

biofuel production and waste management (Gupta et al. 2017; Singh et al. 2017). *Chlorella minutissima* UTEX 2341 had strong resistance to $Cd^{2+}$, $Cu^{2+}$, $Mn^{2+}$, and $Zn^{2+}$ ions under heterotrophic culture conditions and could efficiently eliminate them through intracellular accumulation and extracellular immobilization (Yang et al. 2015). Lipid accumulation in algal cells was not inhibited by HMs. The algal lipid content was significantly increasing by 21 and 94% with the addition of $Cd^{2+}$ and $Cu^{2+}$, respectively (Yang et al. 2015). At low concentrations, HMs such as $Pb^{2+}$, $Al^{3+}$, and $Co^{2+}$ exhibited stimulatory effects on the growth of *Dunaliella tertiolecta* and *Monoraphidium minutum*. Arsenate was found to support the growth of cyanobacterium (*Nostoc minutum*) and microalgae *Chlorella salina* and *Chlorella* sp. (Miazek et al. 2015). Table 6 presents the influence of HMs on the lipid contents of algae.

Higher HMs (namely, $Cu^{2+}$ and $Cd^{2+}$) concentrations affect *Amphora coffearformis* by reducing its growth and biochemical compositions (Anantharaj et al. 2011). Table 7 summarizes the impacts of HMs on the carbohydrate contents of algae. Metals in small concentrations are vital for algae cells to achieve cellular functions. They act as

**Table 6** Effects of heavy metals (HMs) on algal lipid

| Algae strain | Metal | HM concentration | Lipid content | Reference |
|---|---|---|---|---|
| *Amphora coffeaeformis* | $Cu^{2+}$ | 0.2–10 mg $L^{-1}$ | 90–200 µg $L^{-1}$ | Anantharaj et al. (2011) |
| | $Cd^{2+}$ | 0.2–10 mg $L^{-1}$ | 120–170 µg $L^{-1}$ | |
| *Anabaena oryzae* | Fe | 3.77 mg $L^{-1}$<br>2.56 mg $L^{-1}$ | 23.6 mg $g^{-1}$ DCW | Fawzy and Issa (2016) |
| | $Pb^{2+}$ | 0.064 mg $L^{-1}$<br>0.038 mg $L^{-1}$ | | |
| | $Cu^{2+}$ | 0.071 mg $L^{-1}$<br>0.049 mg $L^{-1}$ | | |
| | $Mn^{2+}$ | 0.068 mg $L^{-1}$<br>0.057 mg $L^{-1}$ | | |
| *Cyanosarcina fontana* | Fe | 3.77 mg $L^{-1}$<br>2.56 mg $L^{-1}$ | 11.0 mg $g^{-1}$ DCW | |
| | $Pb^{2+}$ | 0.064 mg $L^{-1}$<br>0.038 mg $L^{-1}$ | | |
| | $Cu^{2+}$ | 0.071 mg $L^{-1}$<br>0.049 mg $L^{-1}$ | | |
| | $Mn^{2+}$ | 0.068 mg $L^{-1}$<br>0.057 mg $L^{-1}$ | | |
| *Pavlova viridis* | $Cu^{2+}$ | 3.0 mg $L^{-1}$ | 2000 × nmol $10^6$ $Cells^{-1}$ | Li et al. (2006) |
| | $Zn^{2+}$ | 6.5 mg $L^{-1}$ | 700 × nmol $10^6$ $Cells^{-1}$ | |
| *Chlorella vulgaris* | Fe | $1.2 \times 10^{-5}$ mol $L^{-1}$ | 56.6% DCW | Liu et al. (2008) |
| *Scenedesmus quadricauda* | $Cd^{2+}$ | 0.1 mM | 62.5 mg $g^{-1}$ DCW | Issa et al. (2016) |
| *Nannochloropsis salina* | As | 1X: 0.078 mg $L^{-1}$<br>40X: 3.12 mg $L^{-1}$ | 1X: 23%<br>40X: 26% | Torres et al. (2017) |
| | $Cd^{2+}$ | 1X: 0.015 mg $L^{-1}$<br>40X: 0.6 mg $L^{-1}$ | 1X: 26%<br>40X: 22% | |
| | Cr | 1X: 0.13 mg $L^{-1}$<br>40X: 5.2 mg $L^{-1}$ | 1X: 24%<br>40X: 26% | |
| | $Co^{2+}$ | 1X: 0.016 mg $L^{-1}$<br>40X: 0.64 mg $L^{-1}$ | 1X: 23%<br>40X: 20.5% | |
| | $Cu^{2+}$ | 1X: 0.13 mg $L^{-1}$<br>40X: 5.2 mg $L^{-1}$ | 1X: 25%<br>40X: 21% | |
| | $Pb^{2+}$ | 1X: 0.054 mg $L^{-1}$<br>40X: 2.16 mg $L^{-1}$ | 1X: 25%<br>40X: 22% | |
| | $Ni^{2+}$ | 1X: 0.25 mg $L^{-1}$<br>40X: 10 mg $L^{-1}$ | 1X: 25%<br>40X: 29% | |
| | Hg | 1X: 0.01 mg $L^{-1}$<br>40X: 0.4 mg $L^{-1}$ | 1X: 24%<br>40X: 22% | |
| | Se | 1X: 0.01 mg $L^{-1}$<br>40X: 0.4 mg $L^{-1}$ | 1X: 23%<br>40X: 22% | |
| | $Zn^{2+}$ | 1X: 0.44 mg $L^{-1}$<br>40X: 17.6 mg $L^{-1}$ | 1X: 23.5%<br>40X: 24% | |

**Table 7** Effects of HMs on algal carbohydrate

| Algae strain | HM | HM concentration | Carbohydrate content | References |
|---|---|---|---|---|
| *Amphora coffeaeformis* | $Cu^{2+}$ | 0.1–10 mg $L^{-1}$ | 330–450 µg $L^{-1}$ | Anantharaj et al. (2011) |
| | $Cd^{2+}$ | 0.2–10 mg $L^{-1}$ | 340–380 µg $L^{-1}$ | |
| *Chlorella vulgaris* | $Co^{2+}$ | $10^{-9}$ M | 300 µg $mg^{-1}$ DCW | Afkar et al. (2010) |
| | $Cu^{2+}$ | $10^{-9}$ M | 270 µg $mg^{-1}$ DCW | |
| | $Zn^{2+}$ | $10^{-9}$ M | 310 µg $mg^{-1}$ DCW | |
| *Scenedesmus quadricauda* | $Cd^{2+}$ | 0.1 mM | 126.1 mg $g^{-1}$ DCW | Issa et al. (2016) |

*DCW* dry cell weight

components for photosynthetic electron transport proteins ($Fe^{3+}$ and $Cu^{2+}$) and photosynthetic water oxidizing centers ($Mn^{2+}$) and are elements in vitamins ($Co^{2+}$). They also serve as co-factors for enzymes participating in CO2 fixation ($Zn^{2+}$ in carbonic anhydrase) (Moroney et al. 2001), DNA transcription ($Zn^{2+}$ in RNA polymerase), and phosphorus acquisition ($Zn^{2+}$ in alkaline phosphatase) (Sunda 2012). Table 8 summarizes the effects of HMs on algal protein contents.

## Biotechnological improvements of phycoremediation process for HM depilation

Phycoremediation is a part of environmental biotechnology that uses algae to treat contaminants (Amit et al. 2017; Apandi et al. 2019). One emerging research area is the design and development of new algal strains with increased affinity, capacity, and selectivity for biosorption of HM ions (Apandi et al. 2019). Biological mechanisms have been manipulated at the molecular level to develop new biosorbents and to produce genetically modified algae with higher biosorption capacity and selectivity for specific metal ions (Fig. 6). The high cost of conventional approaches using wild algae to decrease toxic metal ions concentrations in water to acceptable regulatory standards has stimulated exploration of genetic and protein-engineering methods to produce cost-effective 'green' biosorbents (Abedi 2019; Ansari et al. 2019; Rajamani et al. 2007). Many genes are involved in metal-uptake, detoxification, and tolerance of HMs toxicity (Mrudula et al. 2016). Manipulation of cysteine-rich peptides such as glutathione (GSH), lipopolysaccharides (LPSs), phytochelatins (PCs), and metallothioneins (MTs) that bind metal ions (e.g., Cd, Cu, and Hg) has been suggested for improvement of metal ions bioaccumulation (Godlewska-Zylkiewicz 2001). Tripeptide GSH, a low-molecular-weight thiol, plays a major role in metal ions detoxification by acting as storage for endogenous S and N (Gharieb and Gadd 2004). The genetic manipulation strategy has recently been adopted to increase cell surface MTs or PCs in order to increase the metal ions accumulation capacity of algal cells.

The algal biomass that is commercially available is not produced for phycoremediation applications, and thus may not exhibits optimal performance. The use of dead biomass compromises the phycoremediation capacities of living cultures, particularly when dealing with low concentrations of HMs. The currently available approaches of immobilization have not proven to be satisfactory for large-scale

**Table 8** Effects of HMs on algal protein

| Algae strain | HM | HM concentration | Protein content | References |
|---|---|---|---|---|
| *Amphora coffeaeformis* | $Cu^{2+}$ | 0.2–10 mg $L^{-1}$ | 220–360 µg $L^{-1}$ | Anantharaj et al. (2011) |
| | $Cd^{2+}$ | 0.2–10 mg $L^{-1}$ | 200–250 µg $L^{-1}$ | |
| *Spirulina platensis–S5* | $Pb^{2+}$ | 0.05–0.2 mg $L^{-1}$ | 15–100% | Torres et al. (2017) |
| | $Cu^{2+}$ | 0.05–0.2 mg $L^{-1}$ | 50–90% | |
| | $Zn^{2+}$ | 0.05–0.2 mg $L^{-1}$ | 40–100% | |
| *Gracilaria domingensis* | $Cd^{2+}$ | 100–300 µmol | 20–30 nmol $min^{-1}$ $mg^{-1}$ | Rodrigo et al. Rodrigo et al. (2012) |
| *Chlorella vulgaris* | $Co^{2+}$ | $10^{-9}$ M | 0.6 µg $mg^{-1}$ DCW | Afkar et al. (2010) |
| | $Cu^{2+}$ | $10^{-9}$ M | 0.7 µg $mg^{-1}$ DCW | |
| | $Zn^{2+}$ | $10^{-9}$ M | 1.4 µg $mg^{-1}$ DCW | |
| *Pavlova viridis* | $Cu^{2+}$ | 0.05 mg $L^{-1}$ | $5.3 \times 10^6$ $Cells^{-1}$ | Li et al. (2006) |
| | $Zn^{2+}$ | 0.65 mg $L^{-1}$ | $3.2 \times 10^6$ $Cells^{-1}$ | |
| *Scenedesmus quadricauda* | $Cd^{2+}$ | 0.1 mM | 38.1 mg $g^{-1}$ DCW | Issa et al. (2016) |

*DCW* dry cell weight

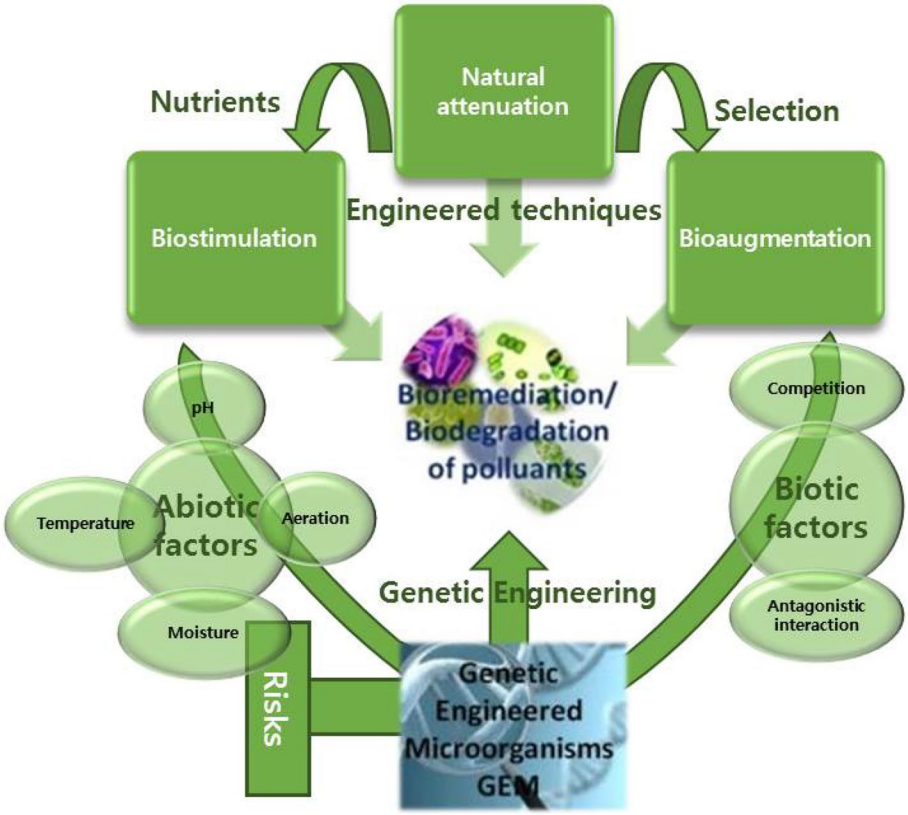


**Fig. 6** Capacities of microorganisms for bioremediation and biodegradation constitute forms of natural attenuation. However, these capacities may be improved by engineering techniques, either by addition of selected microorganisms (bioaugmentation) or by addition of nutrients (biostimulation). Genetic engineering is also used to develop the biodegradation abilities of microorganisms (Joutey et al. 2013)

applications, due to insufficient biomass production. There are many variables and parameters need to be considered for design and operation of phycoremediation, such as algal selection, containment types with contacting time, biomass recovery, disposal of spent biomass, and economic considerations for overall process.

## Conclusion

HMs contamination of aquatic eco-systems is a matter of great concern because of its toxicity towards plants, animals, and human health. Various algal species have been recognized as promising candidates for HMs removal and/or detoxification, and potential low-cost alternatives to physicochemical remediation techniques. HMs removal can be achieved by biosorption and bioaccumulation. The efficiency of HMs removal by algae is influenced by several parameters including pH, temperature, ionic strength, contact time, and presence of counter ions. The supplementation of phytohormones improves algal resistance to HMs toxicity. The genetic manipulation of algae has developed HM-tolerant mutant strains with high specificity and metal removal efficiency. This review directs future research toward the development of a sustainable technology through algal bioremediation for simultaneous treatment of HM-rich wastewaters and massive production for producing biofuel.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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