Chapter 3
Removal of Heavy Metals and Organic Pollutants by Marine Microalgae

Jagannathan Umamaheswari, Ricky Rajamanickam, Sowmya Vilvanathan, Subramanian Shanthakumar, Kadiyala Venkateswarlu, Sudharsanam Abinandan, and Mallavarapu Megharaj

Abstract Marine environment is a predominant player in the overall ecosystem functioning with almost half of oxygen evolution into the atmosphere through the photosynthetic activity of plankton communities. Anthropogenic activities cause pollution at an enhanced pace and pose a major threat to the biological cyclings in the marine ecosystem. Pollutants such as heavy metals and organic compounds in the marine environment are a serious concern as they are associated with complex challenges. Marine microalgae are promising candidates in remediating inorganic and organic pollutants due to their versatile metabolic mechanisms. The present chapter provides a comprehensive understanding of the response of marine microalgae in the removal of heavy metals and organic pollutants. Initially, we present the importance of microalgae and the sources of heavy metals and organic pollutants that reach the marine environment besides highlighting the merits and demerits of the conventional and biological treatment systems used for the removal of these pollutants. Finally, we provide a general perspective on the implication of

J. Umamaheswari · R. Rajamanickam · S. Vilvanathan · S. Shanthakumar
Department of Environmental and Water Resources Engineering, School of Civil and Chemical Engineering, VIT University, Vellore, India

K. Venkateswarlu
Formerly Department of Microbiology, Sri Krishnadevaraya University, Anantapuramu, India

S. Abinandan
Global Centre for Environmental Remediation (GCER), College of Engineering, Science and Environment, University of Newcastle, Callaghan, NSW, Australia

M. Megharaj (✉)
Global Centre for Environmental Remediation (GCER), College of Engineering, Science and Environment, University of Newcastle, Callaghan, NSW, Australia

CRC CARE, Newcastle University LPO, Callaghan, NSW, Australia
e-mail: megh.mallavarapu@newcastle.edu.au

© The Author(s), under exclusive license to Springer Nature Switzerland AG 2023

T. Encarnação, A. Canelas Pais (eds.), *Marine Organisms: A Solution to Environmental Pollution?*, Environmental Challenges and Solutions,
https://doi.org/10.1007/978-3-031-17226-7_3

marine microalgae and the associated mechanisms in the removal of heavy metals and organic pollutants.

Keywords Marine microalgae · Heavy metals · Organic pollutants · Bioremediation

3.1 Introduction

The environment is the global ecological life-supporting system that has been affected in complex and accelerating ways because of pervasive and profound human activities. The past few decades witnessed rapid industrial development, population growth, economic wealth, and urbanization, which ultimately disturb the very processes and components of the nature. Marine ecosystems are at serious risk due to the elevated levels of pollutants discharged from industrial and domestic activities (Bergmann et al. 2015; Nelms et al. 2017). The impact of these pollutants on coastal zone has been significantly greater in estuaries due to their residence time than in inland rivers (Saldarriaga-Hernandez et al. 2020). In fact, the occurrence of both heavy metals and organic pollutants in the marine environment is of significant ecological concern. International scientific experts on marine protection define marine pollution as "chemicals introduced by human activities either directly or indirectly into the marine environment affecting the biota and impairment of water quality" (Kuppusamy et al. 2020). Fish inhabiting polluted waters was reported to accumulate metals in the tissues and the accumulation depends on various biotic and abiotic factors (Zeitoun and Mehana 2014). The heavy metals tend to be widely distributed in liver, kidney, and other tissues and potentially get transferred to humans as they are at the top of the food web (Gabriel et al. 2006). Oils are the major sources of organic contaminants released into the marine environment either during processing or accidentally from drilling, production, and storage (Kuppusamy et al. 2020). Consequently, the deteriorated health of the oceans around the world impacted the social and economic status and prompted to bring international options for safer and healthier marine systems (Gelcich et al. 2014).

Several environmental agencies recognized the severity of these pollutants and proposed various policies in reducing the risk toward marine biota. For instance, a list of priority pollutants that should be universally avoided has been prepared as they can cause shorter or longer effects in any ecosystem (Grip 2017; Beiras 2018). The United States Environmental Protection Agency recently updated the priority pollutant list in the Clean Water Act, which includes several heavy metals, organic contaminants such as dyes, phenols, organophosphates, etc. (USEPA 2014). The United Nations Convention on Law of Sea proposed major duties for member states to investigate potential threats in the marine environment (Stelzenmüller et al. 2018). European Commission endorsed the marine strategy framework directive with an aim to manage Europe-bound seas to gain a healthy state following an ecosystem-based approach (Borja et al. 2013; Danovaro et al. 2016). Marine environments contain several biotas together with marine microalgae that serve as the primary producers and can also be used as sensitive bioindicators (Torres et al. 2008). This

chapter highlights the implication of marine microalgae in the removal of heavy metals and organic pollutants.

3.2 Marine Microalgae—An Overview

Marine environments are inhabited by assemblages of several organisms (Tragin and Vaulot 2018). The diversity of marine plankters based on their size is presented in Fig. 3.1. They are easily distinguished based on the nutrition mode: autotrophic organisms, referred to as phytoplankton (microalgae), and grazing organisms, called zooplankton. In addition, marine microalgae are the major primary producers in the marine environment that use solar energy for CO_2 uptake, thus contributing to ocean carbon sink (Huang et al. 2017). These microalgae are generally divided into two

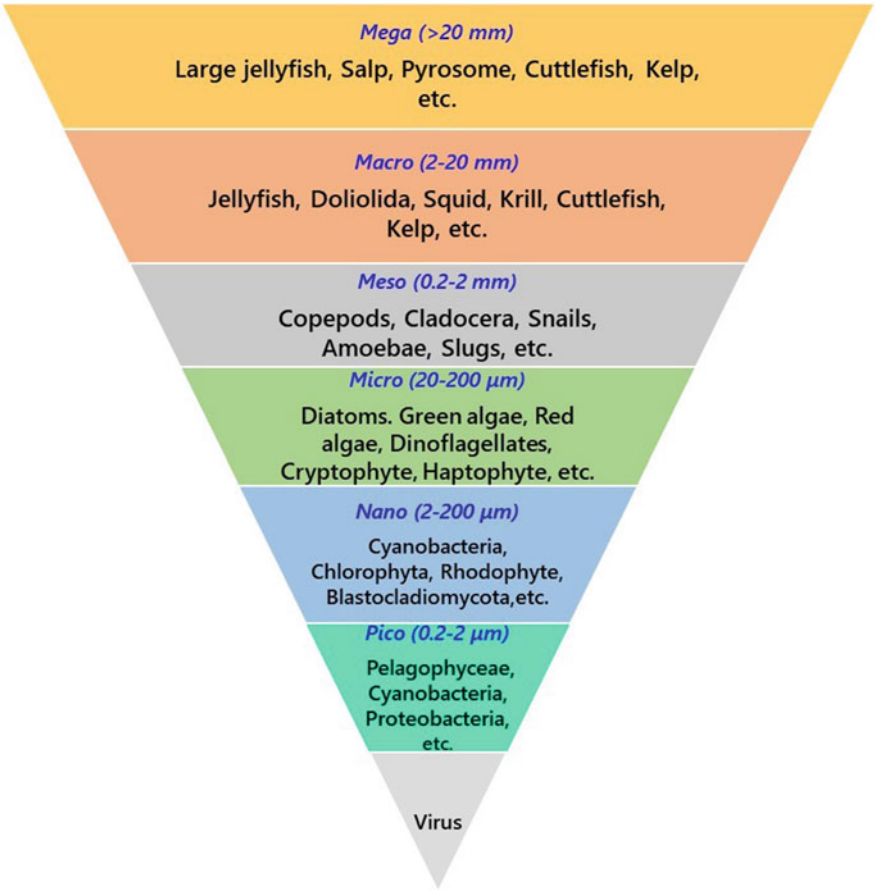

Fig. 3.1 Diversity and classification of marine plankters based on their sizes

lineages such as green and red, with the former being originated by primary and the latter from the secondary or tertiary endosymbiotic process (Nakayama et al. 1998). Chlorophyta is the major algal group in marine waters representing the green lineage, whereas the protists and dinoflagellates fall within the red lineage. Chlorophyta encompasses prasinophytes and chlorophytes, where the abundance is dominated later with *Ulvophyceae*, *Trebouxiophyceae*, and *Chlorophyceae*, all known as the UTC Clade (Leliaert et al. 2012; Fučíková et al. 2014). Chlorophyta consists of chloroplasts surrounded by two membranes with chlorophyll *b* as the major pigment. Parsinophytes comprise eight lineages of different taxonomic levels, and the numbers increase based on the environmental sequences and novel cultures (Tragin and Vaulot 2018). Chlorophyceae alone comprises two thousand species and are well known for several biotechnological applications (Barra et al. 2014). For example, microalgal biomass is reported to yield several primary metabolites such as carotenoids, proteins, lipids, and polyunsaturated fatty acids (Becker 2004; Guedes et al. 2011; Sharma et al. 2012; Christaki et al. 2013). Due to their biomass productivity and surface ratio, microalgae also play a crucial role in biogeochemical cycling of pollutants in marine waters (Van Gestel and Van Brummelen 1996). For example, the cell wall composition of microalgae is reported to have greater capacity for the metal-binding that can be transferred to food chain through grazing (Wang et al. 1998).

Due to the abundance of microalgae in waters, they have been overwhelmingly considered as sensitive bioindicators to monitor pollutants in the marine environment (Levine 1984; Whitton and Kelly 1995; Ali et al. 1999; Volterra and Conti 2000). While thoroughly reviewing the toxic profile of marine algae, Torres et al. (2008) proposed that the widespread abundance of microalgae in the marine environment can be used for seasonal evaluation or the effect of time change in the ecosystem in response to heavy metals and organic pollutants. Owing to the presence of these pollutants, microalgae tend to respond through physiological changes. Reports indicate that among other marine plankton, diatoms are severely affected by pollutants than green microalgae (Harrison et al. 1986; González et al. 2009). In addition, the green marine microalgae are reported to often dominate the bloom of natural population in the marine environment, particularly at increased pollution levels (Bonin et al. 1986; Folgar et al. 2009). Microalgae are known to respond to pollutants through two mechanisms: accumulation and sorption, and they also synthesize phytochelatins that are responsible for metal detoxification (Gekeler et al. 1988; Folgar et al. 2009). Furthermore, the antioxidants and innate enzymes have been shown to detoxify organic pollutants (Sunda et al. 2002; Stahl and Sies 2003; Sharma et al. 2012). Despite their versatile biochemical mechanisms, a detailed understanding of metal and organic pollutant removal by marine microalgae is very limited. The following sections present a comprehensive overview on the role of marine microalgae in the removal of heavy metals and organic pollutants.

3.3 Pollution in the Marine Environment—Sources of Heavy Metals and Organics

Anthropogenic sources of heavy metals and organic pollutants in the marine ecosystem generally result from the direct discharge of wastes, water runoff, and airborne pollutants (Leprovost 2001). These pollutants are carried from inland through sewage, dredged spoil, rainwater, and domestic and industrial waste discharged into coastal waterbodies through estuaries that enter the oceans (Wu et al. 2001; Adeniji et al. 2017). Hydrocarbon pollution is one of the great threats to the marine environment, with estimates of discharge accounting for 1–8 million tons per year (National Research Council Committee on Oil in the Sea, 2003). In addition, around 25,000 ship cargo with 18.5 million barrels of oil per day navigates through gulf waters which can potentially result in minor accidental spills causing a threat to the marine environment (Chitrakar et al. 2019). These crude oil spills affect marine organisms by limiting gas exchange and reducing light penetration (González et al. 2009). Moreover, crude oil spills release several organic pollutants such as benzene, toluene, xylene, and aromatic hydrocarbons that can accumulate in marine biota and sediments, thus acting as a sink affecting the ecosystems (Kachel 2008).

The marine environment is also reported to receive copious and stable inputs of pyrogenic hydrocarbons from coal and oil combustion as well as other organic products such as wood (Ravindra et al. 2008; Page et al. 1999). The predominant source of heavy metals in the marine environment is the industrial effluents discharged into the ocean either through runoff or improper disposal. Three types of heavy metals that cause major environmental problems include toxic metals such as cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), nickel (Ni), cobalt (Co), etc., precious metals like silver (Ag), gold (Au), palladium (Pd), platinum (Pt), etc., and radionuclides such as uranium (U), thorium (Th), radium (Ra), etc. (Wang and Chen 2009). Human exposure to heavy metals has dramatically risen because of an exponential increase in their use in several industrial, domestic, agricultural and technological applications. Other potential anthropogenic sources of heavy metal pollution are industrial effluents, acid mine drainage associated with mining operations, and coal-based and nuclear power plants. Various industries produce and discharge different heavy metals at varying concentrations into the environment; few of them include electroplating, metallurgy, surface finishing industries, energy and fuel production, iron and steel manufacturing, lead-acid battery manufacturing, fertilizer and pesticide industry, electrolysis, electro-osmosis, microelectronics, leather manufacturing, electrical appliance manufacturing, photography, etc. (Ahmaruzzaman 2011). Natural phenomena such as weathering of rocks and volcanic eruptions also significantly contribute to heavy metal pollution.

3.4 Removal of Heavy Metals and Organic Pollutants by Marine Microalgae

A comparison of conventional remediation techniques such as chemical precipitation, ion exchange, membrane filtration, electrochemical treatment, coagulation, and flocculation with those of bioremediation approaches, in terms of their merits and demerits (Table 3.1), clearly indicates that remediation of the polluted sites following the conventional engineering approaches is challenging both technically and economically. Also, bioremediation that involves the capabilities of microorganisms in the removal of pollutants is the most promising, relatively efficient, and cost-effective technology. The following sections particularly deal with the innate capabilities of microalgae in the removal of heavy metals and organic pollutants from marine environments.

3.4.1 Removal of Heavy Metals by Marine Microalgae

Abundant occurrence of metals in the environment leads to their increased concentration in the organisms over time. Bioavailability most often refers to the availability of contaminants, such as heavy metals or organic pollutants, in an ecosystem. Frequently, it is also used to determine the potential risk of pollutants toward nontarget organisms in any system. Bioavailability in the environment primarily involves physical, chemical, and biological processes. Contaminants or pollutants may be present in varying forms: (i) associated with soil and or sediment particles (bound form), (ii) released from liquid and or gaseous phases (release form), and (iii) associated with living organisms (attached form). A contaminant enters a liquid or gaseous phase once it is released from the bound phase. During this stage contaminant transport will take place through advection, diffusion, and dispersion, which result in the movement of contaminant molecules in the medium (liquid or gas) and thereby reassociation of contaminant or return to the bound state (soil). Meanwhile, the contaminants are carried to the surface of the living organisms (Fig. 3.1). Similar processes occur in the medium and eventually the contaminant reaches the living organisms and enters their tissues through cell membrane. Thus, contaminant transport is an important component of its bioavailability. The contaminants after their entry into the cells are metabolized and/or excreted, causing adverse or toxic effects to living organisms (Fig. 3.2).

3.4.1.1 Biosorption of Metals

Biosorption is the process of removing sorbet (metal ions) from the solvent (water) using biological material called a biosorbent. Marine microalgae have recently gained attention for the development of biosorbent materials due to their high

Table 3.1 Merits and demerits of available remediation technologies for the removal of heavy metals and organic contaminants

Treatment technology	Treatment process	Heavy metal treatment	Organic contaminant treatment	References
Physico-chemical treatment methods				
Physical separation	The process involves: Mechanical screening, Gravity separator, Magnetic separation, Electrostatic separation, and Attrition scrubbing	*Merits:* Large-size heavy metals can be easily segregated. Easy maintenance and operation.	*Merits:* Organic contaminants that are clogged onto solid wastes such as wood, plastic, etc. can be removed easily. Gravity separation reduces 50–60% of the suspended solids.	Marino et al. (1997), Dermont et al. (2008), Gupta et al. (2012)
		Demerits: Removal efficiency depends upon the particle size distribution, soil-clay matrix, moisture content, metal magnetic properties, and pollutant hydrophobic properties.	*Demerits:* Regular maintenance is required. Screens are clogged frequently.	
Conventional chemical treatment	Chemical precipitation	*Merits:* Heavy metals are precipitated and removed as sludge. Low cost of precipitant. Simplicity. pH can be controlled.	*Merits:* Effective in removing polymeric electrolytes such as carboxyl, phenol, phosphoryl, and sulfonyl groups.	Liao and Randtke (1986), Matlock et al. (2002), Wingenfelder et al. (2005), Özverdi and Erdem (2006), Chen et al. (2018b)
		Demerits: Removal efficiency depends upon the pH, temperature, and charge of heavy metal ions. Metal hydroxides solubility depends upon the pH conditions (8.0–11.0).	*Demerits:* Usage of large proportions of chemicals for precipitations produces a large amount of sludge. Handling of sludge and usage of chemical is costly.	

(continued)

Table 3.1 (continued)

Treatment technology	Treatment process	Heavy metal treatment	Organic contaminant treatment	References
		Toxic sludge. Metal precipitation is slow with poor settling. Sulfide precipitation results in the production of toxic H_2S gas.	pH-dependent. Weakly adsorbing organic pollutants can retard precipitation.	
	Coagulation and flocculation	*Merits:* Sludge settling is faster. Easy dewatering. Sludge stability. Heavy metal concentrations less than 100 mg L^{-1} can be treated.	*Merits:* Higher molecular weight organic contaminants are eliminated easily.	Randtke (1988), Ayoub et al. (2001), Shen et al. (2015), Sakhi et al. (2019)
		Demerits: The use of coagulants increases settling time. High chemical consumption. A large volume of sludge production with toxic properties. pH-dependent (11.0–11.5).	*Demerits:* Removes only selected group of organic contaminants. Produces large quantity of sludge. Molecular weights less than 500 are not effectively removed. Longer settling time.	
	Flotation	*Merits:* Recovery of heavy metals is selective. Low sludge generation. High separation efficiency. Better removal of small particles. Fewer energy requirements.	*Merits:* Simple in operation. Ability to treat a wide range of organic contaminants. Recovery of organic contaminants is possible. Surfactant cost is low.	Hu et al. (2002), Matis et al. (2004), Salmani et al. (2013)

		Space requirement is low. Less operating cost.	Effective in treating volatile organic contaminants.	
		Demerits: Removal efficiency is dependent on interfacial chemistry and aggregation effectiveness.	*Demerits:* Surfactant needs to be selected based on the organic contaminants present in the wastewater.	
	Adsorption	*Merits:* Low-cost adsorbents can be used (agricultural waste such as coconut coir pith, orange peel pith, plant-derived biomass). Sludge production is very less. Metal recovery is possible. Higher removal efficiency.	*Merits:* A very effective option for tertiary treatment. Various organic pollutants can be handled. Synthetic organic contaminants are effectively treated.	Anirudhan and Sreekumari (2011), Burakov et al. (2018), Alalwan et al. (2020)
		Demerits: Difficulty in adsorbent regeneration Activated charcoal is efficient in treating the pollutant but costly. Efficiency depends upon the adsorbents.	*Demerits:* Regeneration of adsorbent is difficult. Disposal of adsorbent is costly.	
	Ion-exchange	*Merits:* Ion-exchange resins are soluble in water. Valuable heavy metals can be recovered. Cost-effective. Ease of operation.	*Merits:* Operation is simple. Installation is easy. Usage of anion exchange resins effectively removes natural organic matter.	Bolto et al. (2002), Dąbrowski et al. (2004), Bashir et al. (2019)

(continued)

Table 3.1 (continued)

Treatment technology	Treatment process	Heavy metal treatment	Organic contaminant treatment	References
		Very effective in treating low-concentration heavy metal ions.		
		Demerits: Highly pH sensitive. Matrix gets easily fouled.	*Demerits:* Treatment efficiency depends upon the resins and type of organic contaminants in the wastewater. Loss of capacity of resins with time.	
Electrochemical	The process involves: Electro-deposition, Electro-coagulation, Electro-flotation, and Electro-oxidation	*Merits:* Ease of operation. In situ generation of coagulant. Sludge production is very less. Can be used as an alternative to conventional coagulation treatment. Very high efficiency of the metal removal process.	*Merits:* Both soluble and insoluble organic contaminants can be degraded. Carboxyl functional group pollutants can be treated effectively.	Chen (2004), Cheng et al. (2007), Sun et al. (2009), Tran et al. (2017)
		Demerits: A high proportion of chemicals are required for coagulation and precipitation. A solid waste disposal problem. The time of precipitation depends upon the metal ions. Poor settling. It is not a cost-effective treatment.	*Demerits:* Chlorinated organics create secondary pollution. Energy consumption is high. Compound-specific removal.	

	Electrodialysis	*Merits:* Highly concentrated heavy metal ions can be treated. Suitable for metal ion concentration below 20 mg L^{-1}. Chromium and copper metals ions can be recovered.	*Merits:* Metal-organic complexes can be separated. Reclamation of treated water.	Kongsricharoern and Polprasert (1996), Aydin et al. (2019), Gurreri et al. (2020)
		Demerits: Corrosion problem. Heavy metal concentration higher than 1000 mg L^{-1} cannot be effectively treated. Periodic maintenance. Operation is not simple.	*Demerits:* Organic contaminants induce fouling. Very efficient only when the concentration of NaCl is low. Energy consumption is high.	
Advanced treatment methods				
Membrane filtration	Ultra-filtration (UF), and Micellar-enhanced ultra-filtration (MEUF) Polymer-enhanced ultra-filtration (PEUF)	*Merits:* More than 90% removal efficiency Ions concentration with 10–112 mg L^{-1} can be treated. pH 5–9.5 can be handled. Smaller space requirement for installation. Recovery of heavy metals.	*Merits:* Usage of chemicals is avoided. No hazardous by-products. High separation efficiency for organic complexes in the wastewater.	Molinari et al. (2008), Landaburu-Aguirre et al. (2010), El Zeftawy and Mulligan (2011), Isawi (2019)
		Demerits: Membrane replacement. Removal efficiency depends upon the concentration of metals and surfactants for MEUF. Heavy metal concentration and type of polymer used in treating effects PEUF. Operating cost is high. Only efficient when the pH	*Demerits:* Membrane easily fouled by natural organic contaminants. The operating cost is high.	

(continued)

Table 3.1 (continued)

Treatment technology	Treatment process	Heavy metal treatment	Organic contaminant treatment	References
		condition of the wastewater is above 6.		
	Complexation-ultra-filtration	*Merits:* High separation selectivity. Water-soluble polymer ligands. Lower energy requirements. Higher bonding selectivity. Metal concentrates can be reused. The complexing agent can be easily regenerated and reused.	*Merits:* Simultaneous removal of organic pollutants and heavy metal complexes. Lower energy requirement. Removes trace organic contaminants effectively. The binding capacity of polymeric complexing agents.	Trivunac and Stevanovic (2006), Siyanytsya et al. (2008), Borbély and Nagy (2009), Garba et al. (2019)
		Demerits: Efficiency depends upon complexation agent. Condition of membrane determines the metal removal process. Membrane fouling. The presence of salt affects the membrane surface charge reducing the efficiency.	*Demerits:* Ultrafiltration efficiency decreases when organic pollutant complex increases.	
	Reverse osmosis (RO)	*Merits:* Many types of ions, as well as bacteria, can be removed. Membrane pore size is less than 2 nm. 90–99% removal efficiency.	*Merits:* Trace organic pollutants are easily removed. 97% removal efficiency for ionic contaminants. Membrane availability is plentiful.	Ipek (2005), Yangali-Quintanilla et al. (2011), Rodrigues Pires da Silva et al. (2016)
		Demerits: Separation efficiency depends upon the concentration, pressure,	*Demerits:* Membrane fouling.	

		and water flux rate. High power consumption. Frequent membrane replacement. High-quality feed is required or else the membrane will be fouled by colloidal matters in the wastewater.	Energy consumption is high. Post-treatment is necessary.	
Advanced oxidation methods	Fenton oxidation	*Merits:* Higher degradation efficiency. Flexible in operation.	*Merits:* Enhances biodegradability. Faster mineralization of organic pollutants in the wastewater.	Pérez et al. (2002); Bautista et al. (2008); Nguyen et al. (2021)
		Demerits: Disposal of ferric sludge is not easy. pH-dependent. Catalyst is required in large dosages. Hydroxyl and Carboxyl groups formed in Fenton oxidation can form larger heavy metal ion species.	*Demerits:* Disposal of ferric sludge is not easy. Pre-treatment is required to completely degrade the organic pollutants. pH-dependent.	
	Electrochemical Fenton oxidation	*Merits:* In situ production of H_2O_2. Negligible formation of secondary pollutants. Ability to handle higher concentration of wastewater. A clean and effective way. Does not require additional oxidant.	*Merits:* Very effective in treating recalcitrant organic pollutants. Highly reactive.	Kabdaşli et al. (2010), Anawar and Ahmed (2019), Song et al. (2019), Magro et al. (2020)
		Demerits: Low treatment efficiency. Treatment of heavy metals	*Demerits:* Frequent maintenance is required.	

(continued)

Table 3.1 (continued)

Treatment technology	Treatment process	Heavy metal treatment	Organic contaminant treatment	References
		depends upon the current density and pH. Oxidant concentration generated is relatively low.	Wide ranges of organic contaminants cannot be treated. pH-sensitive.	
	Photocatalytic oxidation	*Merits:* Widely used in the removal of heavy metal complexes. UV radiation can be used in the disinfection process as well. Solar energy can be utilized.	*Merits:* Effective polishing step. Taste and odor-causing organic pollutants such as pesticides, geosmin, and methyl tert-butyl ether are effectively oxidized.	Antoniadis et al. (2010), Chen et al. (2017), Brillas (2020)
		Demerits: Depends upon the characteristics of metal ions. Efficient UV illumination in large-scale treatment is inefficient.	*Demerits:* Bulk organic content and high turbidity requires a high UV dosage. Not cost-effective.	
	Ozonation	*Merits:* High removal efficiency. Improvement of wastewater biodegradability.	*Merits:* Lower ozone dose requirement. Very efficient. Aromatic compounds, alkenes, and certain pesticides are effectively removed by ozone.	Clark et al. (1988), Xia and Hu (2018), Honarmandrad et al. (2020)
		Demerits: The low solubility of ozone in water. Energy consumption is high to produce ozone. Low oxidation efficiency.	*Demerits:* Ozone solubility depends upon pH. Alkanes are treated poorly. Expensive treatment technology.	

	Discharge plasma oxidation	*Merits:* High reactivity and can be operated without chemical reagents.	*Merits:* Very effective in treating pesticides 90% removal in 5 minutes. High concentration of pollutants can be treated.	Magureanu et al. (2018), Wang et al. (2017), Liu et al. (2020)
		Demerits: High energy consumption and operating cost. Handling of this technology is complex.	*Demerits:* Degrading efficiency depends upon the molecular structure of the target pollutants. Unstable organic peroxides are formed.	
Biological treatment methods				
Activated sludge	The process involves: Bacteria, Aeration, and Agitation	*Merits:* Sludge is re-circulated back continually. Metals like iron and lead are efficiently removed by the process.	*Merits:* Acid and lipophilic compounds are biodegradable and treated effectively. Biodegradation is the major removal mechanism.	Oliver and Cosgrove (1974), Pagnanelli et al. (2009), Karpińska and Kotowska (2019)
		Demerits: Toxic sludge and disposal of sludge is problematic. Large area and proper maintenance.	*Demerits:* High toxic contaminants cannot be treated. The concentration of pollutants should be low enough to support bacterial life. Trace organic compounds are poorly treated by activated sludge.	
Trickling filters	The process involves: Aeration, Coarse media (stone or plastic), and Micro-organisms	*Merits:* Various types of filter media (gravel media or plastic media) are available for effective	*Merits:* Surfactants polluted water are effectively treated. Energy consumption is less.	Dermou et al. (2007), Ziolko et al. (2009), Katam et al. (2020)

(continued)

Table 3.1 (continued)

Treatment technology	Treatment process	Heavy metal treatment	Organic contaminant treatment	References
		treatment. The bacterial population can be easily maintained and controlled. Very effective. Economical process for industrial wastewater treatment. The use of chemicals is avoided.	Biofilm culture (algal-bacteria consortia) enhances the removal efficiency of the filters. Organic matters are easily biodegraded.	
		Demerits: High probability of clogging. High capital cost. Microbial community is affected by toxic metals. Not effective as activated sludge process in treating heavy metals.	*Demerits:* Longer retention time is needed. Toxic contaminants affect the micro-organism population.	
Stabilization ponds	The process involves: Constructed shallow basins, and Micro-organisms	*Merits:* Various types of heavy metal ions can be treated. Very cheap and easy to operate.	*Merits:* A low concentration of organic contaminants is removed effectively. 60% removal efficiency for trace organic pollutants such as caffeine and naproxen.	Polprasert and Charnpratheep (1989), Jasper et al. (2013), Gad and Abdalla (2017), Qaderi et al. (2019)
		Demerits: Slow and inefficient in removing heavy metal ions. Depends upon the interaction of micro-organisms, sunlight, and oxygen. Water source is one of the	*Demerits:* Time-consuming process. Wide range of organic contaminants cannot be treated.	

		limiting factors. Not suitable for all geographic areas only for arid and semi-arid zones.		
Biosorption	The process involves: Adsorption, and Precipitation	*Merits:* Simple in operation and high efficiency. Agricultural by-products can be used as adsorbents (rice husk, pecan shells, maize cob, rice straw, rice husk, coconut shell). Low cost of adsorbents and regeneration of bio sorbent. Usage of dead biomass reduces the need for nutrient supplication.	*Merits:* Simple and cheap compared to advanced treatment technologies. Ability to treat multicomponent organic contaminants. High selectivity of treatment. Less sludge is generated.	Chaukura et al. (2016), Ramírez Calderón et al. (2020)
		Demerits: Removal efficiency depends completely upon the cellulose, lignin, carbohydrate, and silica properties present in the adsorbents. A sudden change in pH and temperature affects the efficiency of the bio sorbent. Decrease in binding sites with usage.	*Demerits:* Disposal of biowaste (spent bio sorbent). Putrefaction of biomass under moist conditions. Limited regeneration capacity of bio sorbents.	
Biopolymers	Biopolymer adsorbent	*Merits:* Widely used in industries capable of reducing metal ions concentration to parts per billion. Low cost and higher removal	*Merits:* Biopolymers such as chitin and chitosan are renewable and biodegradable. Very effective in the treatment of	Vidal and Moraes (2019); Zia et al. (2020)

(continued)

Table 3.1 (continued)

Treatment technology	Treatment process	Heavy metal treatment	Organic contaminant treatment	References
		efficiency. Abundant availability and biodegradability of biopolymers.	phenolic compounds and pesticides (80–90% removal).	
		Demerits: Rapid degradability of biopolymers.	*Demerits:* The selection of biopolymers is based upon the pollutant load in the wastewater. Removal efficiency depends upon the ionic strength of the organic pollutant, pH, contact time, and temperature.	

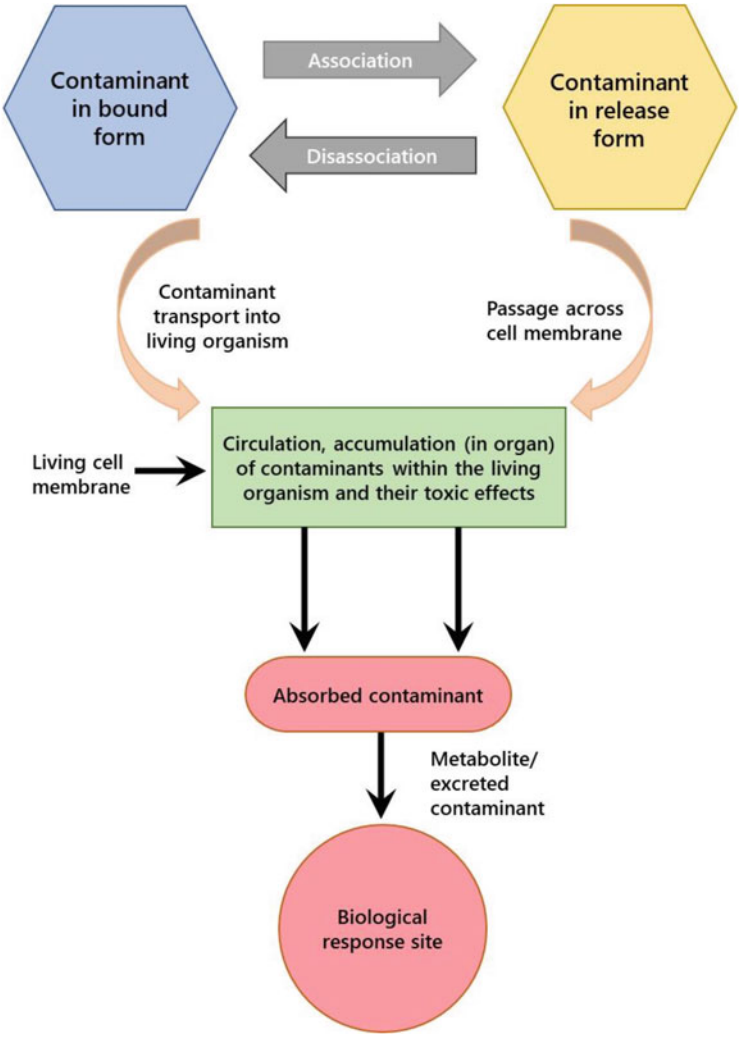

Fig. 3.2 Fate of the contaminants after their entry into the cell system

sorption capacity and availability in seas and oceans. Due to the presence of alkaline metal ions in the composition of algal cell walls the heavy metal ions in the water can be easily treated through a simple ion-exchange process. These sorbents have the metal-sequestering property that can be used to reduce the concentration of heavy metal ions in the solvent from parts per million (ppm) to parts per billion (ppb) level. Biosorption capacity determines the number of metal ions that microalgae can bind on the surface, and it is denoted by q_{max}. Brinza et al. (2007) reviewed the biosorption capacity of some marine microalgal species involving the commonly detected heavy metals found in the wastewater, as shown in Table 3.2.

Table 3.2 The maximum heavy metal biosorption capacity of some marine microalgal species (based on data from Brinza et al. 2007)

Marine microalga	Biosorption capacity q_{max} (mmol g^{-1})				
	Heavy metal				
	Pb	Cd	Ni	Zn	Cu
Chlorella sp.	0.46	0.44	0.31	0.18	0.55
Chlorococcum sp.	0.23	0.15	0.27	0.21	0.36
Cyclotella cryptica	0.42	–	0.14	0.1	0.33
Spirogyra sp.	0.49	0.27	0.12	0.23	0.53
Lyngbya taylorii	0.84	0.32	0.43	0.37	–
Microcystis aeruginosa	0.35	–	0.21	0.23	0.37
Scendesmus sp.	0.45	0.11	–	0.35	0.22

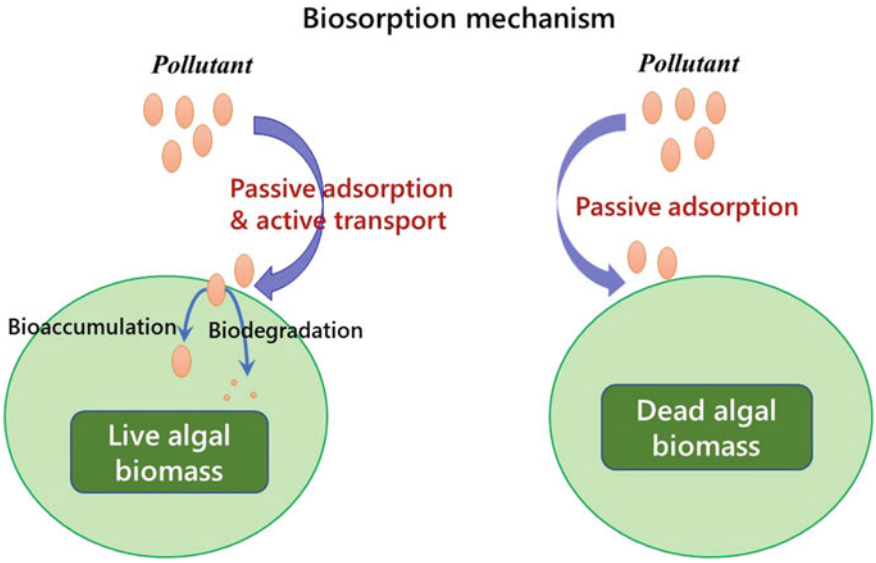

Fig. 3.3 Biosorption of pollutants in marine microalgae

Biosorption is an extracellular process that is carried out in the cell membrane in which the algal biomass binds the heavy metals in the cell wall. The algal cell wall is composed of polysaccharides that contain sulfate. Imidazole, phosphate, hydroxyl, amine, and amino functional groups act as a binding site for the heavy metals to be adsorbed. The biosorption mechanism (Fig. 3.3) can be divided into metabolism-dependent biosorption in which transportation of the pollutant across the cell membrane takes place, followed by intercellular accumulation or detoxification. Metabolism-independent mechanisms involve ion exchange, complexation, chelation, and precipitation process. For example, the cell wall of microalgae is composed of polysaccharides, lipids, and proteins that provide many functional groups capable of attracting both anionic and cationic heavy metal ions exchanging them with the

functional groups present in the cell wall. While investigating the mechanism for removing Cr^{3+}, Cd^{2+}, and Cu^{2+} by *Spirulina*, Chojnacka et al. (2005) found that hydroxyl, carboxyl, and phosphate functional groups were involved in the removal of the metal ions by the ionic-exchange process. Similarly, a microalgal strain, *Tetraselmis marina* AC16-MESO, could remove Cu (90%), Fe (100%), and Mn (50%) after 72-h incubation period, mostly by complexation of metal ions onto functional groups at the cell surface (Cameron et al. 2018). In fact, complexation mechanism is the result of electrostatic attraction between heavy metal ions and organic molecules present on the cell which act as ligands. The complex formation between the metal ion and ligand is due to the covalent bonds. The functional group (phosphonate, carboxyl, and amine) present in the cell wall of *Chlorella miniate* removed Cr^{3+} by the complexation process (Han et al. 2006). Organic acids such as citric, fumaric, lactic, oxalic and gluonic have been found to chelate metal ions resulting in the formation of metallo-organic complexes. Chelation is the advanced form of complexation mechanism in which the metal ion would bond with a ligand in many positions at the same time with higher stability. *Chlamydomonas reinhardtii* removed Hg^{2+} by direct chelation mechanism in which glutathione not only adsorbed the metal ion but also reduced the toxicity of the pollutant in water (Perales-Vela et al. 2006).

Two marine algae, *Chlorella* sp. and *Phormidium* sp., exposed to tannery wastewaters removed Cr concentration by 81 and 90%, respectively, at the end of 15 days incubation period as revealed by metabolic mechanism (Das et al. 2018). When the metal ion solubility decreases, the bioavailability is reduced, resulting in the mechanism of precipitation. Upon exposure to the heavy metal-polluted medium, the algal biomass favored precipitation that was based on pH of the medium. If pH of the medium increases, the active sites on the cell wall attract heavy metal ions. Cu, Ag, and Pb ions were removed by the alga, *Tertaselmis suecica*, by the mechanism of precipitation due to the presence of phosphates on the cellular surface (Ballan-Dufrançais et al. 1991). While growing *Chlorella* sp. in seawater-based medium, nearly 4% of Cd supplemented was found precipitated due to an increase in pH to 8 besides 67% accumulation and 25% adsorption of the metal (Matsunaga et al. 1999).

3.4.1.2 Factors Influencing Biosorption of Heavy Metals

Biotic Factors

Algal Species Marine microalgae can be classified into three broad categories based on the composition of pigment color in green algae (Chlorophyta), red algae (Rhodophyta), brown algae (Phaeophyta) (Davis et al. 2003). Romera et al. (2007) summarized the biosorption capacity of algae related to some heavy metals as indicated in Table 3.3. Brown algae have a higher sorption capacity than red and green algae due to their high alginate content and the presence of functional groups in the structure. But the use of brown and red marine algae has a major drawback due

Table 3.3 Average heavy metal sorption capacity (q_{max}), in mmol g^{-1}, of different algae (data based on Romera et al. 2007)

Phylum	Cadmium	Nickel	Zinc	Copper	Lead
Chlorophyta	0.60	0.51	0.37	0.50	0.80
Rhodophyta	0.20	0.27	–	–	0.65
Phaeophyta	0.90	0.84	0.67	1.01	1.23

to the presence of certain organic compounds such as alginate. Also, the pigments generate secondary pollutants and reduce the biosorption capacity. In green algae the secondary pollutant generation is insignificant but their biosorption capacity is lower as compared to brown and red algae. While studying the impact of biotic factors on Cu adsorption capacity in marine microalgae, Levy et al. (2007) observed that *Dunaliella tertiolecta* was least sensitive than *Minutocellus polymorphus* and was depended on uptake rates across cell membrane rather than the taxonomic status and cell size.

Concentration of Biomass In the biosorption process, the removal efficiency depends upon the biomass concentration because of the greater availability of binding sites on the cell surface. Increased biomass concentration enhances the removal percentage of heavy metals. An increase in biomass concentration of *Ulva fasciata* from 0.5 to 4 g L^{-1} resulted in the improvement of Pb removal efficiency in the range of 42–75%, while the removal efficiency of Cd increased from 43 to 73% with the increase in biomass concentration from 0.5 to 6 g L^{-1} (Nessim et al. 2011). Increased biomass concentration often reduces the biosorbent capacity of microalgae because of the reduction in intercellular distance and cell agglomeration. Kaparapu and Prasad (2018) observed higher biosorption of Cd(II) in *Nannochloropsis oculata* with biomass concentration of 7 g L^{-1} and a decrease in biosorption capacity with increased biomass concentration probably due to the partial biomass aggregation that results in surface area reduction.

Tolerance Algal species are known to grow, adapt, and tolerate hazardous environmental conditions. Heavy metal tolerance in algae depends upon the algal species. However, members of Chlorophyceae are generally known to tolerate Cu^{2+}, Zn^{2+}, and Cd^{2+}. Strains of *Chlorella* sp. isolated from mercury-contaminated sites tolerated higher Hg^{2+} concentration than the isolates from uncontaminated habitats (Gaur and Rai 2001). Pérez-Rama et al. (2010) observed 87% of Cd accumulation in a marine microalga, *T. sueccia*, and was related to phytochelatin synthesis. Folgar et al. (2009) reported that *Dunaliella salina* was tolerant to higher concentrations of Cd due to the intracellular metal-binding ligands.

Surface Area to Volume Ratio The ratio of surface area to volume in microalgae influences the sequestration of heavy metals in the solution. The take-up nutrients, in terms of per biomass, are faster in microalgae than macroalgae because of the size, growth, metabolism, and biochemical composition (Hein et al. 1995). Khoshmanesh et al. (1997) reported that the uptake of Cd was similar in an algal species having different sizes. The microalgal culture with a specific surface area of 2.20 m^2 mg^{-1}

cells showed higher uptake of Cd ions as compared to the culture with a specific surface area of 0.98 m^2 mg^{-1} cells.

Abiotic Factors

pH Biosorption of heavy metals in solution depends upon pH conditions due to the functional groups that dissociate at certain pH levels in the algal biomass. The maximum sorption of heavy metal ions by the marine microalgal biomass was obtained at a pH range between 4.0 and 6.0. The observed percentage removal efficiency for Cr, Cd, As, Pb, and Hg at pH 6.0 were 98.30, 92.50, 96, 92.20, and 80, respectively (Kumar et al. 2020; Leong and Chang 2020). When the pH value is lower than 6.0, the hydrogen ion concentration does not compete with the metal ions, and during adsorption of heavy metals no vacant active sites are created in the algal biomass (Gupta et al. 2011). If the pH value is greater than 6.0, the metal species are hydrolysed and are no longer available for the biosorption process (Romera et al. 2007). Kaparapu and Prasad (2018) reported that the biosorption of Cd(II) at pH >7 was reduced in a marine microalga, *Nannochloropsis* sp., and at pH 2–4 there was a competition between metal ions and metal-binding sites located on algal cell surface. The reduced Cd biosorption at higher pH was attributed to the maximum immobilization of positive charges. When the initial pH was maintained at 7.8, the cells of *T. suecica* were metabolically active and increased in cell number from 30 to 40 mg g^{-1} within 48 h, suggesting that the live cells are more suitable for biosorption than dead cells (Pérez-Rama et al. 2010).

Temperature Temperature plays a vital role in the biosorption process as it influences the process in both positive and negative ways depending upon the range in temperature (Khambhaty et al. 2009). The solubility of metal ions was found to be higher at elevated temperatures, but an increase in temperature decreases the biosorption capacity of the biomass. The maximum biosorption of Cu^{2+} ions attained at 37 °C was 90% in *Spirulina* species but the biosorption capacity was reduced to 82% at 60 °C and then gradually decreased with further increase in temperature (Al-Homaidan et al. 2014). The biosorption efficiency of *N. oculata* biomass increased with contact time up to 90 min and remained constant (Kaparapu and Prasad 2018).

Contact Time The efficiency of biosorption process depends upon the contact time between the algal biomass and the heavy metal ion. It was observed that the optimum contact time for the maximum adsorption of 80–90% of Cu, As, Cd, Cr, Pb, and Hg by various marine algal species was within 60–90 min (Al-Homaidan et al. 2014; Leong and Chang 2020). Initially, many active sites are available on the cell surface for the adsorption of heavy metals, and there will be a reduction in active sites with time, resulting in a gradual decline in the removal capacity of biomass that requires regeneration of algal biomass. The amount of biosorbed Cd in *D. salina* biomass was greater after 24-h contact time and was subsequently reduced due to the enhanced sorption onto the cellular surface (Folgar et al. 2009). It has been reported that

biosorption yield of Cd(II) decreased with increased temperature at an optimal contact time due to the following reasons: relative increase in leaching tendency of ions from solid phase to bulk phase, and weakness of active sites for biosorption in the sorbed phase (Kaparapu and Prasad 2018).

3.4.1.3 Desorption of Heavy Metals and Biomass Regeneration

Desorption of heavy metals is the process of recovering valuable metal ions from the algal biomass by adding eluent. The eluent restores the biosorbent to its original state for the reuse of biomass in the process. Mineral acids, complexing agents, and organic acids are used as the eluents as they are non-damaging to the sorbent, and they ensure the metal-binding capacity of microalgae. Desorption of Cr^{3+}, Cd^{2+}, and Cu^{2+} from biomass of *Spirulina* sp. by nitric acid resulted in 98% removal of the metal ions (Chojnacka et al. 2005). In fact, *Chlorella vulgaris* remains unaffected even after five cycles of biomass regeneration using 0.1 M EDTA as eluent to recover Cd metal ions, and the adsorption capacity loss was less the 5.8% (Kumar et al. 2018). Both HCl and EDTA are the most used eluents for desorbing algal biosorbents. However, HCl decreases biosorption capacity of algal biomass after every wash, and the use of EDTA is not eco-friendly as it dissolves alginate upon every use which can lead to secondary pollution. Therefore, it is essential to screen the desorbing agents for efficient metal ion recovery.

3.4.1.4 Heavy Metal Detoxification by Marine Microalgae

The ability of microalgae to adapt and survive in habitats contaminated with heavy metals and organic pollutants depends on genetic adaptation which enables them to develop defence mechanisms to resist and adapt the harsh environmental conditions (Nayaka et al. 2017). This mechanism of defence allows microalgae to develop some tolerance and resistance toward the pollutant that can detoxify the pollutants inside the cell. The defence mechanism involves the production of short-chained polypeptides such as phytochelatins (PCs) and metallothioneins (MTs) that are abundant in sulfhydryl and carboxyl groups and can bind to the pollutants (Cobbett and Goldsbrough 2002). The bound pollutant further moves in for internal detoxification process which involves conjugation of the pollutant with the polypeptides and further compartmentalization of the pollutants by transporting them into the vacuoles (Qin et al. 2006). Folgar et al. (2009) reported that metal complexing ligands in *D. salina* were rich in cystine although most of the known are GSH and PCs. They observed that levels of cystine synthesis led to maximum Cd accumulation intracellularly. In another study, *D. salina* was shown to be resistant to As which exhibited higher levels of lipid peroxidation with a differential expression of 65 proteins involved in energy metabolism, protein synthesis and folding, ROS scavenging, and amino acid synthesis (Ge et al. 2016). Wang et al. (2017) reported variation in thiols such as cysteine, glutathione, and PCs in *D. salina* exposed to arsenite and

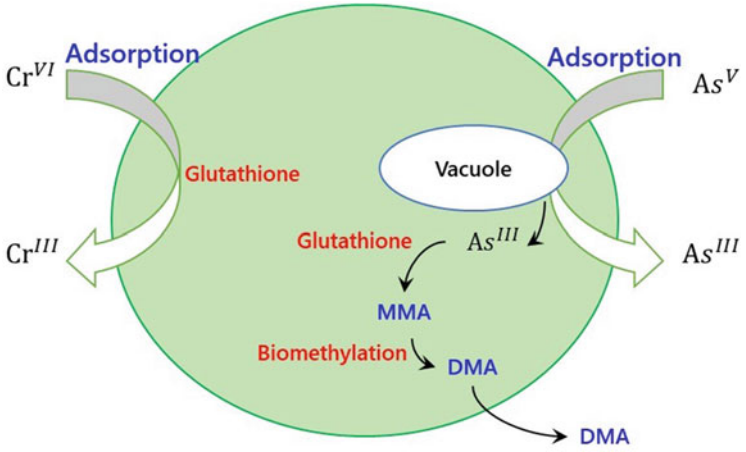

Fig. 3.4 Biotransformation mechanism for heavy metal detoxification in microalgae. MMA, Monomethylarsonic acid; DMA, Dimethylarsinic acid (Source: National Research Council 2003)

demonstrated that transformation of arsenite-induced several PCs initially and later decreased under various phosphate regimes. The synthesis of PCs varied with As (V) and As(III) which affected GSH levels, suggesting that the conversion of GSH to PCs is essential for arsenite mitigation (Wang et al. 2017). The biochemical mechanisms involved in heavy metal detoxification by microalgae (National Research Council 2003) are presented in Fig. 3.4. Sathasivam and Ki (2019) observed higher levels of phytoene synthase (PSY), phytoene desaturase (PDS), and β-lycopene cyclase (LCY-B) in *T. suecica* exposed to copper.

3.4.2 Removal of Organic Pollutants by Marine Microalgae

Human attempts to produce various organic compounds to protect many lives and support economic advantages significantly resulted in acute and chronic toxicity of some of these chemical substances making the biota deteriorate rapidly (Adeola 2004). Although these organic compounds are susceptible to degradation at a very slow process, they tend to persist in the environment or accumulate inside the biota (Subashchandrabose et al. 2013). Organic pollutants that are widely distributed in marine environments and prone to biodegradation by marine microalgae include phenolics, pesticides, persistent organic pollutants (POPs), and hydrocarbons (Dsikowitzky et al. 2011).

3.4.2.1 Pesticides

Pesticides including insecticides, fungicides, and herbicides are often detected in marine waters due to the urban or agriculture runoff causing serious threats to the marine biota. Atrazine sensitivity, in terms of 96-h growth inhibition, for the estuarine phytoplankter, *D. tertiolecta*, in nutrient-replete media was 159.16 μg L^{-1} and was influenced by the duration and nutrient-limited conditions (Flood et al. 2018). Chen and Jiang (2011) reported enhanced catalase activity in *D. salina* when exposed to trichlorfon and dimehypo at lower concentrations of 0.025 g L^{-1} and 0.0005 g L^{-1}, respectively. In a toxicity study involving treatment of *D. salina* with dimethylphenol and dinitroaniline, Zhu and Jiang (2009) observed that the EC_{50} values were significantly higher when exposed to a single pesticide compared to their combination. However, increased concentrations led to significant inhibition in the growth of the microalga that was attributed to the effect on osmosis of cell membrane allowing toxicants to react with internal parts and damage membrane lipids. Thakkar et al. (2013) exposed *D. tertiolecta* and a brown tide alga, *Aureococcus anophagefferens,* to various concentrations of metachlor and observed a significant increase in cell size with glutathione production as detoxification mechanism. Although 40–50% of sublethal concentration of tributylin (TBT) could be removed by *N. oculata* and *Dunaliella parava* during 2–6 days of incubation, the former microalga adsorbed most of the added anti-fouling agent while the latter degraded it to mono-butyltin and di-butyltin (Taha et al. 2009). DeLorenzo and Serrano (2003) determined the toxicity of atrazine, chlorpyrifos, and chlorothalonil individually and as mixtures on *D. tertiolecta* and observed that atrazine and chlorothalonil concentrations at 25 and 33 μg L^{-1} decreased growth rate, while chlorpyrifos was toxic only at >400 μg L^{-1}. In another study, the effect of herbicides such as diuron, irgarol, atrazine, and ametryn was tested toward *D. tertiolecta* in four different scenarios of increased temperature and salinity and reported that increasing temperature reduced growth but enhanced the contents of chlorophyll and starch and lipids (DeLorenzo et al. 2013).

3.4.2.2 Hydrocarbons

Water soluble fraction of crude oil containing mono- and diaromatic hydrocarbons affected *D. tertiolecta* within 24 h though photosynthesis impairment and cell division inhibition occurred. Despite the well-known tolerance of *Dunaliella* species, the exponential phase measured in terms of photosynthesis was reduced while lag phase showed growth inhibition, suggesting that duration of exposure influenced the overall growth (Siron et al. 1991). Fabregas et al. (1984) reported stimulation in the growth of *T. suecica* upon exposure to low hydrocarbon concentrations in crude oil whereas the dispersant did not exhibit any selective toxicity. Dunstan et al. (1975) observed that low concentration (10 mg L^{-1}) of oil had no effect on the growth of *D. tertiolecta*. Similarly, low concentration (0.05%) of light diesel and an oil

dispersant (0.005%), either alone or in combination stimulated the growth of *Chlorella salina* and impaired respiration (Chan and Chiu 1985). Photosynthesis in *D. tertiolecta* exposed to oil samples from tanker spill was significantly affected within 60 min, while survival of the cells was slightly affected (Carrera-Martinez et al. 2011). Jiang et al. (2002) exposed microalgal strains to four PAHs, viz., toluene, naphthalene, 2-methylnapthalene, and phenanthrene, and reported that *C. vulgaris* and *Platymonas subcordiformis* were least sensitive compared to other tested species.

Exposure of *Chlorella salina* to phenanthrene significantly increased the toxicity with an EC_{50} value that ranged from 1.893 to 0.23 mg L^{-1}, and a decrease in pH from 9 to 6 was also significantly toxic suggesting that the acidification of sweater greatly influenced the effect of organic compounds (Chen et al. 2018a). Bretherton et al. (2018) observed that marine alga, *D. tertiolecta*, was resistant to oil and dispersant and referred to it as "robust" because chlorophyll was not affected during lag phase and was followed by biomass accumulation. Moreover, short-term exposure of *D. tertiolecta* to petroleum and diesel oil impacted the growth and photosynthetic performance and reported to recover during long-term incubation (Romero-lopez et al. 2012). Recently, Salinas-Whittaker et al. (2020) observed that *D. tertiolecta* exposed to water-soluble fraction (WSF) from fuel oil/diesel mixture increased physiological and biochemical response in unsaturated acyl chain of fatty acid suggesting the uptake of hydrocarbons. Mohammady et al. (2005) exposed *Nannochloropsis salina* to various concentrations (0–100%) of diesel fuel oil aqueous extract and observed a decrease in cell bioavailability leading to cell division and enhanced membrane permeability. Both the limitation of carbon and hormesis phenomenon, as evaluated by stable isotope analysis, were prevalent in *Platymonas helgolandica* when it was treated with water accommodated fraction of fuel oil (Liu et al. 2020). Dissolved crude oil at lower concentration (20 mg L^{-1}) stimulated the growth of *Dicrateria* sp. but growth was inhibited with increased exposure time. However, consortia of marine microalgae involving *Dicrateria* sp. on biotreated seawater showed enhanced cell density that ranged from 4.0×10^5 to 1.7×10^6 cells mL^{-1}. Chao et al. (2012) reported that four fuel oils, viz., F120, F180, F380, and F20 were toxic to a marine alga, *Chlorella* sp., due to the concentration of several PAHs. Hing et al. (2011) demonstrated that *C. salina* was able to tolerate diesel concentrations at steady state and was only affected when the concentration exceeded 170 mg L^{-1}. Very recently, Marques et al. (2021) reported that *N. oculata* was able to grow in petroleum-contaminated water exhibiting a PAH removal efficiency of 94%. In particular, the percentage removal of several organic compounds such as naphthalene, benzopyrene, and acenaphthylene was 89–99% due to their intracellular biodegradation by oxidoreductase enzymes.

3.4.2.3 Other Organic Compounds

Phenol is an organic compound that results from the transformation of aromatic compounds via degradation, oxidation, and synthesis. Besides being enriched in coal

tar, phenol is also produced as a by-product from several industrial processes as well as during organic matter decomposition (Michalowicz and Duda 2007). Mofeed and Abdel-Aal (2015) found that exposure of *D. salina* to various concentrations (50–-200 μmol L^{-1}) of phenol significantly affected antioxidant enzyme activities. Phenol at a concentration of 72 mg L^{-1} led to programmed cell death in marine microalgae by inducing changes in ultrastructure with shrinkage of the nucleolus and vacuole enlargement (Duan et al. 2017). During treatment of real refinery wastewater containing phenol and its derivatives such as *o*-cresol and *p*-cresol, marine alga, *Nannochloropsis* sp., removed >80% of both the cresols as compared to freshwater *Chlorella* sp. (Surkatti and Al-Zuhair 2018). The biodegradation was reported to occur in two steps: split in methyl group resulting in its conversion to methanol and further breakdown of phenol produced as an intermediate (Papazi et al. 2012). Bisphenol A, with production estimates of approximately two million tons, is well distributed in the environment and known for its endocrine disruption potential (Burridge 2003). While reporting the first toxicity data of chlorophenols on *D. tertiolecta*, Ertürk and Saçan (2012) reported that toxicity of chlorophenols decreased between 48 and 96 h due to the increase in pH of the medium or acclimation response of the marine microalga to the toxicants. Regardless of the exposure time, the toxicity was greater with an increasing number of chlorine atoms, while *ortho*-substituted chlorophenol was lesser than *meta* and *para* congeners (Ertürk and Saçan 2012). POPs are widely distributed due to domestic and industrial activities that are reported to reach marine environments (ter Schure et al. 2004; Lema et al. 2007). Polybrominated diphenyl ethers (PBDEs), the flame retardants, enhanced oxidative stress in *D. salina* with increased activities of superoxide dismutase, catalase, and glutathione reductase and decreased glutathione peroxidase activity (Zhao et al. 2017). Similarly, exposure of *D. salina* to dibutyl phthalate at 100 mg L^{-1} decreased glutathione peroxidase and superoxide dismutase (Wei et al. 2021).

3.5 Conclusions

Besides highlighting the advantages of the use of marine microalgae for the removal of heavy metals and organic pollutants, we presented the inherent drawbacks of the conventional treatment processes. Marine microalgae respond to heavy metals in several ways such as biosorption and bioaccumulation; however, there is a very clear paucity of data on organic contaminant removal and the associated mechanisms. Furthermore, it is very clear that marine microalgae can offer sustainable approach in the treatment of heavy metals and organic pollutants for safer marine ecosystem and biomass production from microalgae after detoxification. Thus, this chapter presents the overall understanding of the potential of marine microalgae in the removal of heavy metals and organic pollutants.

References

Adeniji AO, Okoh OO, Okoh AI (2017) Petroleum hydrocarbon profiles of water and sediment of Algoa Bay, Eastern Cape, South Africa. Int J Environ Res Public Health 14:1263

Adeola FO (2004) Boon or bane? The environmental and health impacts of persistent organic pollutants (POPs). Hum Ecol Rev 11:27–35

Ahmaruzzaman M (2011) Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. Adv Colloid Interface Sci 166:36–59

Alalwan HA, Kadhom MA, Alminshid AH (2020) Removal of heavy metals from wastewater using agricultural byproducts. J Water Supply Res Technol - AQUA 69:99–112

Al-Homaidan AA, Al-Houri HJ, Al-Hazzani AA et al (2014) Biosorption of copper ions from aqueous solutions by *Spirulina platensis* biomass. Arab J Chem 7:57–62

Ali MB, Tripathi RD, Rai UN, Pal A, Siugh SP (1999) Physico-chemical characteristics and pollution level of Lake Nainital (UP, India): role of macrophytes and phytoplankton in biomonitoring and phytoremediation of toxic metal ions. Chemosphere 39:2171–2182

Anawar HM, Ahmed G (2019) Combined electrochemical-advanced oxidation and enzymatic process for treatment of wastewater containing emerging organic contaminants. In: Mishra AK, Anawar HMD, Drouiche NBT-E, NC in W (eds) Emerging and nanomaterial contaminants in wastewater: advanced treatment technologies. Elsevier, pp 277–307

Anirudhan TS, Sreekumari SS (2011) Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons. J Environ Sci 23:1989–1998

Antoniadis A, Takavakoglou V, Zalidis G et al (2010) Municipal wastewater treatment by sequential combination of photocatalytic oxidation with constructed wetlands. Catal Today 151:114–118

Aydin MI, Yuzer B, Hasancebi B, Selcuk H (2019) Application of electrodialysis membrane process to recovery sulfuric acid and wastewater in the chalcopyrite mining industry. Desalin Water Treat 172:206–211

Ayoub GM, Semerjian L, Acra A et al (2001) Heavy metal removal by coagulation with seawater liquid bittern. J Environ Eng 127:196–207

Ballan-Dufrançais C, Marcaillou C, Amiard-Triquet C (1991) Response of the phytoplanctonic alga *Tetraselmis suecica* to copper and silver exposure: vesicular metal bioaccumulation and lack of starch bodies. Biol Cell 72:103–112

Barra L, Chandrasekaran R, Corato F, Brunet C (2014) The challenge of ecophysiological biodiversity for biotechnological applications of marine microalgae. Mar Drugs 12:1641–1675

Bashir A, Malik LA, Ahad S et al (2019) Removal of heavy metal ions from aqueous system by ion-exchange and biosorption methods. Environ Chem Lett 17:729–754

Bautista P, Mohedano AF, Casas JA et al (2008) An overview of the application of Fenton oxidation to industrial wastewaters treatment. J Chem Technol Biotechnol 83:1323–1338

Becker W (2004) Microalgae in human and animal nutrition. In: Richmond A (ed) Handbook of microalgal culture. Blackwell, Oxford, UK, pp 312–351

Beiras R (2018) Marine pollution: sources, fate and effects of pollutants in coastal ecosystems. Chapter 11. Vol. 5, 187–204

Bergmann M, Gutow L, Klages M (2015) Marine anthropogenic litter. Springer Nature, p 447

Bolto B, Dixon D, Eldridge R et al (2002) Removal of natural organic matter by ion exchange. Water Res 36:5057–5065

Bonin DJ, Droop MR, Maestrini SY, Bonin MC (1986) Physiological features of six micro–algae to be used as indicators of seawater quality. Cryptogamie Algol 7:23–83

Borbély G, Nagy E (2009) Removal of zinc and nickel ions by complexation-membrane filtration process from industrial wastewater. Desalination 240:218–226

Borja A, Elliott M, Andersen JH et al (2013) Good environmental status of marine ecosystems: what is it and how do we know when we have attained it? Mar Pollut Bull 76:16–27

Bretherton L, Williams A, Genzer J et al (2018) Physiological response of 10 phytoplankton species exposed to Macondo oil and the dispersant, Corexit. J Phycol 54:317–328

Brillas E (2020) A review on the photoelectro-Fenton process as efficient electrochemical advanced oxidation for wastewater remediation. Treatment with UV light, sunlight, and coupling with conventional and other photo-assisted advanced technologies. Chemosphere 250:126198

Brinza L, Dring MJ, Gavrilescu M (2007) Marine micro and macro algal species as biosorbents for heavy metals. Environ Eng Manag J 6:237–251

Burakov AE, Galunin EV, Burakova IV et al (2018) Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: a review. Ecotoxicol Environ Saf 148:702–712

Burridge E (2003) Bisphenol a: product profile. Eur Chem News April 14–20:17

Cameron H, Mata MT, Riquelme C (2018) The effect of heavy metals on the viability of *Tetraselmis marina* AC16-MESO and an evaluation of the potential use of this microalga in bioremediation. PeerJ 25:e5295

Carrera-Martinez D, Mateos-Sanz A, Lopez-Rodas V, Costas E (2011) Adaptation of microalgae to a gradient of continuous petroleum contamination. Aquat Toxicol 101:342–350

Chan KY, Chiu SY (1985) The effects of diesel oil and oil dispersants on growth, photosynthesis, and respiration of *Chlorella salina*. Arch Environ Contam Toxicol 14:325–331

Chao M, Shen X, Lun F, Shen A, Yuan Q (2012) Toxicity of fuel oil water accommodated fractions on two marine microalgae, *Skeletonema costatum* and Chlorella spp. Bull Environ Contam Toxicol 88:712–716

Chaukura N, Gwenzi W, Tavengwa N, Manyuchi MM (2016) Biosorbents for the removal of synthetic organics and emerging pollutants: opportunities and challenges for developing countries. Environ Dev 19:84–89

Chen G (2004) Electrochemical technologies in wastewater treatment. Sep Pur Tech 38:11–41

Chen H, Jiang J-G (2011) Toxic effects of chemical pesticides (trichlorfon and dimehypo) on *Dunaliella salina*. Chemosphere 84:664–670

Chen H, Zhang Z, Tian F et al (2018a) The effect of pH on the acute toxicity of phenanthrene in a marine microalgae *Chlorella salina*. Sci Rep 8:17577

Chen Q, Yao Y, Li X et al (2018b) Comparison of heavy metal removals from aqueous solutions by chemical precipitation and characteristics of precipitates. J Water Process Eng 26:289–300

Chen Y, Zhao X, Guan W et al (2017) Photoelectrocatalytic oxidation of metal-EDTA and recovery of metals by electrodeposition with a rotating cathode. Chem Eng J 324:74–82

Cheng H, Xu W, Liu J et al (2007) Pretreatment of wastewater from triazine manufacturing by coagulation, electrolysis, and internal microelectrolysis. J Hazard Mater 146:385–392

Chitrakar P, Baawain MS, Sana A, Al-Mamun A (2019) Current status of marine pollution and mitigation strategies in arid region: a detailed review. Ocean Sci J 54:317–348

Chojnacka K, Chojnacki A, Górecka H (2005) Biosorption of Cr^{3+}, Cd^{2+} and Cu^{2+} ions by blue-green algae *Spirulina* sp.: kinetics, equilibrium and the mechanism of the process. Chemosphere 59:75–84

Christaki E, Bonos E, Giannenas I, Florou-Paneri P (2013) Functional properties of carotenoids originating from algae. J Sci Food Agric 93:5–11

Clark RM, Fronk CA, Lykins BW (1988) Removing organic contaminants from groundwater. Environ Sci Technol 22:1126–1130

Cobbett C, Goldsbrough P (2002) Phytochelatins and metallothioneins: roles in heavy metal detoxification and homeostasis. Annu Rev Plant Biol 53:159–182

Dąbrowski A, Hubicki Z, Podkościelny P, Robens E (2004) Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. Chemosphere 56:91–106

Danovaro R, Carugati L, Berzano M (2016) Implementing and innovating marine monitoring approaches for assessing marine environmental status. Front Mar Sci 3:213

Das C, Ramaiah N, Pereira E, Naseera K (2018) Efficient bioremediation of tannery wastewater by monostrains and consortium of marine *Chlorella* sp. and *Phormidium* sp. Int J Phytoremediation 20:284–292

Davis TA, Volesky B, Mucci A (2003) A review of the biochemistry of heavy metal biosorption by brown algae. Water Res 37:4311–4330

DeLorenzo ME, Danese LE, Baird TD (2013) Influence of increasing temperature and salinity on herbicide toxicity in estuarine phytoplankton. Environ Toxicol 28:359–371

DeLorenzo ME, Serrano L (2003) Individual and mixture toxicity of three pesticides; atrazine, chlorpyrifos, and chlorothalonil to the marine phytoplankton species *Dunaliella tertiolecta*. J Environ Sci Health B 38:529–538

Dermont G, Bergeron M, Mercier G, Richer-Laflèche M (2008) Metal-contaminated soils: remediation practices and treatment technologies. Pract Period Hazardous, Toxic, Radioact Waste Manag 12:188–209

Dermou E, Velissariou A, Xenos D, Vayenas DV (2007) Biological removal of hexavalent chromium in trickling filters operating with different filter media types. Desalination 211: 156–163

Dsikowitzky L, Nordhaus I, Jenner-sikowitzky L et al (2011) Anthropogenic organic contaminants in water, sediments and benthic organisms of the mangrove—fringed Segara Anakan Lagoon, Java Indonesia. Mar Pollut Bull 62:851–862

Duan W, Meng F, Lin Y, Wang G (2017) Toxicological effects of phenol on four marine microalgae. Environ Toxicol Pharmacol 52:170–176

Dunstan WM, Atkinson LP, Natoli J (1975) Stimulation and inhibition of phytoplankton growth by low molecular weight hydrocarbons. Mar Biol 31:305–310

El Zeftawy MAM, Mulligan CN (2011) Use of rhamnolipid to remove heavy metals from wastewater by micellar-enhanced ultrafiltration (MEUF). Sep Purif Technol 77:120–127

Ertürk MD, Saçan MT (2012) First toxicity data of chlorophenols on marine alga *Dunaliella tertiolecta*: correlation of marine algal toxicity with hydrophobicity and interspecies toxicity relationships. Environ Toxicol Chem 31:1113–1120

Fabregas J, Herrero C, Veiga M (1984) Effect of oil and dispersant on growth and chlorophyll a content of the marine microalga *Tetraselmis suecica*. Appl Environ Microbiol 47:445–447

Flood S, Burkholder J, Cope G (2018) Assessment of atrazine toxicity to the estuarine phytoplankter, *Dunaliella tertiolecta* (Chlorophyta), under varying nutrient conditions. Environ Sci Pollut Res 25:11409–11423

Folgar S, Torres E, Pérez-Rama M et al (2009) *Dunaliella salina* as marine microalga highly tolerant to but a poor remover of cadmium. J Hazard Mater 165:486–493

Fučíková K et al (2014) New phylogenetic hypotheses for the core Chlorophyta based on chloroplast sequence data. Front Ecol Evol 2:63

Gabriel OM, Rita O, Clifford A, Kennedy O (2006) Heavy metal pollution of fish of Qua-Iboe River Estuary: possible implications for neurotoxicity. Int J Toxicol 3:1–6

Gad AAM, Abdalla AMA (2017) Fate of heavy metals and nutrients in waste stabilization ponds in arid zones. JES J Eng Sci 45:1–16

Garba MD, Usman M, Mazumder MAJ et al (2019) Complexing agents for metal removal using ultrafiltration membranes: a review. Environ Chem Lett 17:1195–1208

Gaur JP, Rai LC (2001) Heavy metal tolerance in algae. In: Rai LC, Gaur JP (eds) Algal adaptation to environmental stresses. Springer, Berlin Heidelberg, Berlin, Heidelberg, pp 363–388

Ge Y, Ning Z, Wang Y et al (2016) Quantitative proteomic analysis of *Dunaliella salina* upon acute arsenate exposure. Chemosphere 145:112–118

Gekeler W, Grill E, Winnnacker EL, Zenk MH (1988) Algae sequester heavy metals via synthesis of phytochelatin complexes. Arch Microbiol 150:197–202

Gelcich S, Buckley P, Pinnegar JK et al (2014) Public awareness, concerns, and priorities about anthropogenic impacts on marine environments. Proc Natl Acad Sci 111:15042–15047

González J, Figueiras FG, Aranguren-Gassis M et al (2009) Effect of a simulated oil spill on natural assemblages of marine phytoplankton enclosed in microcosms. Estuar Coast Shelf Sci 83:265–276

Grip K (2017) International marine environmental governance: a review. Ambio 46:413–427

Guedes AC, Amaro HM, Malcata FX (2011) Microalgae as sources of carotenoids. Mar Drugs 9: 625–644

Gupta VK, Ali I, Saleh TA et al (2012) Chemical treatment technologies for waste-water recycling—an overview. RSC Adv 2:6380–6388

Gupta VK, Jain R, Saleh TA et al (2011) Equilibrium and thermodynamic studies on the removal and recovery of safranine-T dye from industrial effluents. Sep Sci Technol 46:839–846

Gurreri L, Tamburini A, Cipollina A, Micale G (2020) Electrodialysis applications in wastewater treatment for environmental protection and resources recovery: a systematic review on progress and perspectives. Membranes 10:1–93

Han X, Wong YS, Tam NFY (2006) Surface complexation mechanism and modeling in Cr(III) biosorption by a microalgal isolate, *Chlorella miniata*. J Colloid Interface Sci 303:365–371

Harrison PJ, Cochlan WP, Acreman JC, Parsons TR et al (1986) The effect of crude oil and Corexit 9527 on marine phytoplankton in an experimental enclosure. Mar Environ Res 18:93–109

Hein M, Pedersen MF, Sand Jensen K (1995) Size-dependent nitrogen uptake in micro- and macroalgae. Mar Ecol Prog Ser 118:247–254

Hing LS, Ford T, Finch P, Crane M, Morritt D (2011) Laboratory stimulation of oil–spill effects on marine phytoplankton. Aquat Toxicol 103:32–37

Honarmandrad Z, Javid N, Malakootian M (2020) Efficiency of ozonation process with calcium peroxide in removing heavy metals (Pb, Cu, Zn, Ni, Cd) from aqueous solutions. SN Appl Sci 2: 703

Hu L, Adeyiga AA, Miamee E (2002) Removal of organic chemicals from wastewater by surfactant separation. United States

Huang Y, Yang X, Lan L, Zhan J, Luo H, Jiang L (2017) Studies on the diversity of marine microalgae and the strains with high polysaccharides, lipids and proteins along Zhanjiang coastal areas. Act Hydrobiol Sinica 41:1080–1090

Ipek U (2005) Removal of Ni(II) and Zn(II) from an aqueous solution by reverse osmosis. Desalination 174:161–169

Isawi H (2019) Evaluating the performance of different nano-enhanced ultrafiltration membranes for the removal of organic pollutants from wastewater. J Water Process Eng 31:100833

Jasper JT, Nguyen MT, Jones ZL et al (2013) Unit process wetlands for removal of trace organic contaminants and pathogens from municipal wastewater effluents. Environ Eng Sci 30:421–436

Jiang Y, Zhihong W, Xiurong H, Lei Z, Xiulin W (2002) Toxicity of polycyclic aromatic hydrocarbons (PAHs) to marine algae. Mar Sci 26:46–50

Kabdaşli I, Arslan T, Arslan-Alaton I et al (2010) Organic matter and heavy metal removals from complexed metal plating effluent by the combined electrocoagulation/Fenton process. Water Sci Technol 61:2617–2624

Kachel MJ (2008) Threats to the marine environment: pollution and physical damage. Particularly Sensitive Sea Areas: The IMO's Role in Protecting Vulnerable Marine Areas, 23–36

Kaparapu J, Prasad MK (2018) Equilibrium, kinetics and thermodynamic studies of cadmium (II) biosorption on *Nannochloropsis oculata*. Appl Water Sci 8:1–9

Karpińska J, Kotowska U (2019) Removal of organic pollution in the water environment. Water (Switzerland) 11

Katam K, Shimizu T, Soda S, Bhattacharyya D (2020) Performance evaluation of two trickling filters removing LAS and caffeine from wastewater: light reactor (algal-bacterial consortium) vs dark reactor (bacterial consortium). Sci Total Environ 707:135987

Khambhaty Y, Mody K, Basha S, Jha B (2009) Biosorption of Cr(VI) onto marine *Aspergillus niger*: experimental studies and pseudo-second order kinetics. World J Microbiol Biotechnol 25: 1413–1421

Khoshmanesh A, Lawson F, Prince IG (1997) Cell surface area as a major parameter in the uptake of cadmium by unicellular green microalgae. Chem Eng J Biochem Eng J 65:13–19

Kongsricharoern N, Polprasert C (1996) Chromium removal by a bipolar electro-chemical precipitation process. Water Sci Technol 34:109–116

Kumar M, Singh AK, Sikandar M (2018) Study of sorption and desorption of cd (II) from aqueous solution using isolated green algae *Chlorella vulgaris*. Appl Water Sci 8:225

Kumar M, Singh AK, Sikandar M (2020) Biosorption of hg (II) from aqueous solution using algal biomass: kinetics and isotherm studies. Heliyon 6:e03321

Kuppusamy S, Maddela NR, Megharaj M, Venkateswarlu K (2020) Fate of total petroleum hydrocarbons in the environment. In: Total Petroleum Hydrocarbons. Springer, Cham, pp 57–77

Landaburu-Aguirre J, Pongrácz E, Perämäki P, Keiski RL (2010) Micellar-enhanced ultrafiltration for the removal of cadmium and zinc: use of response surface methodology to improve understanding of process performance and optimisation. J Hazard Mater 180:524–534

Leliaert F et al (2012) Phylogeny and molecular evolution of the green algae. CRC Crit Rev Plant Sci 31:1–46

Lema SC, Schultz I, Scholz N, Incardona J, Swanson P (2007) Neural defects and cardiac arrhythmia in fish larvae following embryonic exposure to 2,29,4,49-tetrabromodiphenyl ether (PBDE–47). Aquat Toxicol 82:296–307

Leong YK, Chang JS (2020) Bioremediation of heavy metals using microalgae: recent advances and mechanisms. Bioresour Technol 303:122886

LeProvost I (2001) Environmental impact of the offshore oil and gas industry. J Environ Assess Policy Manage 3:173–175

Levine HG (1984) The use of seaweeds for monitoring coastal waters. In: Shubert EL (ed) Algae as Ecological Indicators. Academic Press, London, pp 189–210

Levy JL, Stauber JL, Jolley DF (2007) Sensitivity of marine microalgae to copper: the effect of biotic factors on copper adsorption and toxicity. Sci Total Environ 387:141–154

Liao MY, Randtke SJ (1986) Predicting the removal of soluble organic contaminants by lime softening. Water Res 20:27–35

Liu Y, Li N, Lou Y, Liu Y, Zhao X, Wang G (2020) Effect of water accommodated fractions of fuel oil on fixed carbon and nitrogen by microalgae: implication by stable isotope analysis. Ecotoxicol Environ Safe 195:110488

Magro C, Mateus EP, Paz-Garcia JM, Ribeiro AB (2020) Emerging organic contaminants in wastewater: understanding electrochemical reactors for triclosan and its by-products degradation. Chemosphere 247:125758

Magureanu M, Bradu C, Parvulescu VI (2018) Plasma processes for the treatment of water contaminated with harmful organic compounds. J Phys D Appl Phys 51:313002

Marino MA, Brica RM, Neale CN (1997) Heavy metal soil remediation: the effects of attrition scrubbing on a wet gravity concentration process. Environ Prog 16:208–214

Marques IM, Oliveira ACV, de Oliveira OMC, Sales EA, Moreira ÍTA (2021) A photobioreactor using *Nannochloropsis oculata* marine microalgae for removal of polycyclic aromatic hydrocarbons and sorption of metals in produced water. Chemosphere 281:130775

Matis KA, Zouboulis AI, Gallios GP et al (2004) Application of flotation for the separation of metal-loaded zeolites. Chemosphere 55:65–72

Matlock MM, Howerton BS, Atwood DA (2002) Chemical precipitation of heavy metals from acid mine drainage. Water Res 36:4757–4764

Matsunaga T, Takeyama H, Nakao T, Yamazawa A (1999) Screening of marine microalgae for bioremediation of cadmium-polluted seawater. J Biotechnol 70:33–38

Michalowicz J, Duda W (2007) Phenols–sources and toxicity. Pol J Environ Stud 16:347–362

Mofeed JM, Abdel-Aal EI (2015) Effect of phenol on some antioxidant enzymes in effect of phenol on some antioxidant enzymes in the marine microalga *Dunaliella salina*. J Environ Sci 44:185–196

Mohammady NGED, Chen YC, Mohammad RF (2005) Physiological responses of the eustigmatophycean *Nannochloropsis salina* to aqueous diesel fuel pollution. Oceanologia 47: 75–92

Molinari R, Poerio T, Argurio P (2008) Selective separation of copper(II) and nickel(II) from aqueous media using the complexation-ultrafiltration process. Chemosphere 70:341–348

Nakayama T et al (1998) The basal position of scaly green flagellates among the green algae (Chlorophyta) is revealed by analyses of nuclear-encoded SSU rRNA sequences. Protist 149: 367–380

National Research Council (US) Committee on Oil in the Sea (2003) Oil in the Sea III: Inputs, Fates, and Effects. Washington, DC: National Academies Press

Nayaka S, Toppo K, Verma S (2017) Adaptation in algae to environmental stress and ecological conditions. In: Shukla V, Kumar S, Kumar N (eds) Plant adaptation strategies in changing environment. Springer Singapore, Singapore, pp 103–115

Nelms SE, Coombes C, Foster LC, Galloway TS, Godley BJ, Lindeque PK, Witt MJ (2017) Marine anthropogenic litter on British beaches: a 10-year nationwide assessment using citizen science data. Sci Total Environ 579:399–1409

Nessim RB, Bassiouny AR, Zaki HR et al (2011) Biosorption of lead and cadmium using marine algae. Chem Ecol 27:579–594

Nguyen MK, Tran VS, Pham TT et al (2021) Fenton/ozone-based oxidation and coagulation processes for removing metals (Cu, Ni)-EDTA from plating wastewater. J Water Process Eng 39:101836

Oliver BG, Cosgrove EG (1974) The efficiency of heavy metal removal by a conventional activated sludge treatment plant. Water Res 8:869–874

Özverdi A, Erdem M (2006) Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption from aqueous solutions by pyrite and synthetic iron sulphide. J Hazard Mater 137:626–632

Page DS, Boehm PD, Douglas GS et al (1999) Pyrogenic polycyclic aromatic hydrocarbons in sediments record past human activity: a case study in Prince William sound, Alaska. Mar Pollut Bull 38:247–260

Pagnanelli F, Mainelli S, Bornoroni L et al (2009) Mechanisms of heavy-metal removal by activated sludge. Chemosphere 75:1028–1034

Papazi K, Kotzabasis AK, Kotzabasis K (2012) Bioenergetic strategy for the biodegradation of *p*-cresol by the unicellular green alga *Scenedesmus obliquus*. PLoS One 7:e51852

Perales-Vela HV, Peña-Castro JM, Cañizares-Villanueva RO (2006) Heavy metal detoxification in eukaryotic microalgae. Chemosphere 64:1–10

Pérez M, Torrades F, García-Hortal JA et al (2002) Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions. Appl Catal B Environ 36:63–74

Pérez-Rama M, Torres E, Suárez C, Herrero C, Abalde J (2010) Sorption isotherm studies of Cd (II) ions using living cells of the marine microalga *Tetraselmis suecica* (Kylin) Butch. J Environ Manage 91:2045–2050

Polprasert C, Charnpratheep K (1989) Heavy metal removal in attached-growth waste stabilization ponds. Water Res 23:625–631

Qaderi F, Sayahzadeh AH, Azizpour F, Vosughi P (2019) Efficiency modeling of serial stabilization ponds in treatment of phenolic wastewater by response surface methodology. Int J Environ Sci Technol 16:4193–4202

Qin J, Rosen BP, Zhang Y et al (2006) Arsenic detoxification and evolution of trimethylarsine gas by a microbial arsenite S-adenosylmethionine methyltransferase. Proc Natl Acad Sci U S A 103: 2075–2080

Ramírez Calderón OA, Abdeldayem OM, Pugazhendhi A, Rene ER (2020) Current updates and perspectives of biosorption technology: an alternative for the removal of heavy metals from wastewater. Curr Pollut Rep 6:8–27

Randtke SJ (1988) Organic contaminant removal by coagulation and related process combinations. J Am Water Works Assoc 80:40–56

Ravindra K, Sokhi R, Van Grieken R (2008) Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos Environ 42:2895–2921

Rodrigues Pires da Silva J, Merçon F, Guimarães Costa CM, Radoman Benjo D (2016) Application of reverse osmosis process associated with EDTA complexation for nickel and copper removal from wastewater. Desalin Water Treat 57:19466–19474

Romera E, González F, Ballester A et al (2007) Comparative study of biosorption of heavy metals using different types of algae. Bioresour Technol 98:3344–3353

Romero-Lopez J, Lopez-Rodas V, Costas E (2012) Estimating the capability of microalgae to physiological acclimatization and genetic adaptation to petroleum and diesel oil contamination. Aquat Toxicol 124–125:227–237

Sakhi D, Rakhila Y, Elmchaouri A et al (2019) Optimization of coagulation flocculation process for the removal of heavy metals from real textile wastewater. In: Ezziyyani M (ed) Advances in intelligent systems and computing. Springer International Publishing, Cham, pp 257–266

Saldarriaga-Hernandez S, Hernandez-Vargas G, Iqbal HM, Barcelo D, Parra-Saldívar R (2020) Bioremediation potential of *Sargassum* sp. biomass to tackle pollution in coastal ecosystems: circular economy approach. Sci Total Environ 715:136978

Salinas-Whittaker S, Gómez-Gutiérrez CM, Cordero-Esquivel B, Luque PA, Guerra-Rivas G (2020) Effects of the water-soluble fraction of the mixture fuel oil/diesel on the microalgae *Dunaliella tertiolecta* through growth. Environ Sci Pollut Res 27:35148–35160

Salmani MH, Davoodi M, Ehrampoush MH et al (2013) Removal of cadmium (II) from simulated wastewater by ion flotation technique. Iran J Environ Health Sci Eng 10:16

Sathasivam R, Ki JS (2019) Differential transcriptional responses of carotenoid biosynthesis genes in the marine green alga *Tetraselmis suecica* exposed to redox and non-redox active metals. Mol Biol Rep 46:1167–1179

ter Schure AFH, Larsen P, Agrell C (2004) Atmospheric transport of polybrominated diphenyl ethers and polybrominated biphenyls to the Baltic Sea. Environ Sci Technol 38:1282–1287

Sharma KK, Schuhmann H, Schenk PM (2012) High lipid induction in microalgae for biodiesel production. Energies 5:1532–1553

Shen LC, Nguyen XT, Hankins NP (2015) Removal of heavy metal ions from dilute aqueous solutions by polymer-surfactant aggregates: a novel effluent treatment process. Sep Purif Technol 152:101–107

Siron R, Giusti G, Berland B, Morales-Loo R, Pelletier E (1991) Water–soluble petroleum compounds: chemical aspects and effects on the growth of microalgae. Sci Total Environ 104:211–227

Siyanytsya V, Kochkodan V, Goncharuk V (2008) Natural organic matter removal from water by complexation-ultrafiltration. Desalination 223:91–96

Song Y, Sun T, Cang L et al (2019) Migration and transformation of cu(II)-EDTA during electrodialysis accompanied by an electrochemical process with different compartment designs. Electrochim Acta 295:605–614

Stahl W, Sies H (2003) Antioxidant activity of carotenoids. Mol Asp Med 24:345–351

Stelzenmüller V, Coll M, Mazaris AD, Giakoumi S et al (2018) A risk-based approach to cumulative effect assessments for marine management. Sci Total Environ 612:1132–1140

Subashchandrabose SR, Ramakrishnan B, Megharaj M, Venkateswarlu K, Naidu R (2013) Mixotrophic cyanobacteria and microalgae as distinctive biological agents for organic pollutant degradation. Environ Int 51:59–72

Sun L, Miznikov E, Wang L, Adin A (2009) Nickel removal from wastewater by electroflocculation-filtration hybridization. Desalination 249:832–836

Sunda W, Kieber DJ, Kiene RP, Huntsman S (2002) An antioxidant function for DMSP and DMS in marine algae. Nature 418:317–320

Surkatti R, Al-Zuhair S (2018) Effect of cresols treatment by microalgae on the cells composition. J Water Process Eng 26:250–256

Taha HM, Said HA, Abbas NH, Khaleafa AFM (2009) Biosorption and biodegradation of the antifouling compound tributyltin (TBT) by microalgae. Amer Eur J Sci Res 4:1–6

Thakkar M, Randhawa V, Wei L (2013) Comparative responses of two species of marine phytoplankton to metolachlor exposure. Aquat Toxicol 126:198–206

Torres MA, Barros MP, Campos SC, Pinto E, Rajamani S, Sayre RT, Colepicolo P (2008) Biochemical biomarkers in algae and marine pollution: a review. Ecotoxicol Environ Safe 71: 1–15

Tragin M, Vaulot D (2018) Green microalgae in marine coastal waters: the ocean sampling day (OSD) dataset. Sci Rep 8:1–12

Tran TK, Chiu KF, Lin CY, Leu HJ (2017) Electrochemical treatment of wastewater: selectivity of the heavy metals removal process. Int J Hydrog Energy 42:27741–27748

Trivunac K, Stevanovic S (2006) Removal of heavy metal ions from water by complexation-assisted ultrafiltration. Chemosphere 64:486–491

USEPA (2014) Toxic and Priority Pollutants under the Clean Water Act. (p. Appendix A to Part 423–126 Priority Pollutants). p. Appendix A to Part 423–126 Priority Pollutants. https://www.epa.gov/eg/toxic-and-priority-pollutants-under-cleanwater-act (accessed: January 7, 2020)

Van Gestel CA, Van Brummelen TC (1996) Incorporation of the biomarker concept in ecotoxicology calls for a redefinition of terms. Ecotoxicology 5:217–225

Vidal RRL, Moraes JS (2019) Removal of organic pollutants from wastewater using chitosan: a literature review. Int J Environ Sci Technol 16:1741–1754

Volterra L, Conti ME (2000) Algae as biomarkers, bioaccumulators and toxin producers. Int J Environ Pollut 13:92–125

Wang J, Chen C (2009) Biosorbents for heavy metals removal and their future. Biotechnol Adv 27: 195–226

Wang TC, Weissman JC, Ramesh G et al (1998) Heavy metal binding and removal by *Phormidium*. Bull Environ Contam Toxicol 60:739–744

Wang Y, Zhang C, Zheng Y, Ge Y (2017) Phytochelatin synthesis in *Dunaliella salina* induced by arsenite and arsenate under various phosphate regimes. Ecotoxicol Environ Safe 136:150–160

Wei C, Wang S, Hu X et al (2021) Exposure to dibutyl phthalate induced the growth inhibition and oxidative injury in *Dunaliella salina*. IOP Conference Series: Earth and Environmental Science 804:042038

Whitton BA, Kelly MG (1995) Use of algae and other plants for monitoring rivers. Aust J Ecol 20: 45–56

Wingenfelder U, Hansen C, Furrer G, Schulin R (2005) Removal of heavy metals from mine waters by natural zeolites. Environ Sci Technol 39:4606–4613

Wu Y, Zhang J, Mi TZ, Li B (2001) Occurrence of n-alkanes and polycyclic aromatic hydrocarbons in the core sediments of the Yellow Sea. Mar Chem 76:1–15

Xia Z, Hu L (2018) Treatment of organics contaminated wastewater by ozone micro-nano-bubbles. Water (Switzerland):11

Yangali-Quintanilla V, Maeng SK, Fujioka T et al (2011) Nanofiltration vs. reverse osmosis for the removal of emerging organic contaminants in water reuse. Desalin Water Treat 34:50–56

Zeitoun MM, Mehana EE (2014) Impact of water pollution with heavy metals on fish health: overview and updates. Global Vet 12:219–231

Zhao Y, Wang Y, Li Y, Santschi PH, Quigg A (2017) Response of photosynthesis and the antioxidant defense system of two microalgal species (*Alexandrium minutum* and *Dunaliella salina*) to the toxicity of BDE–47. Mar Pollut Bull 124:459–469

Zhu YH, Jiang JG (2009) Combined toxic effects of typical mutagens–dimethylphenol, tribromethane and dinitroaniline, on unicellular green algae *Dunaliella salina*. J Food Safe 29:1–13

Zia Z, Hartland A, Mucalo MR (2020) Use of low-cost biopolymers and biopolymeric composite systems for heavy metal removal from water. Int J Environ Sci Technol 17:4389–4406

Ziolko D, Hala D, Lester JN, Scrimshaw MD (2009) The effectiveness of conventional trickling filter treatment plants at reducing concentrations of copper in wastewaters. Sci Total Environ 407:6235–6241