Minireview

Harmful Cyanobacterial Blooms (HCBs): innovative green bioremediation process based on anti-cyanobacteria bioactive natural products

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Abstract

Over the last decades, Harmful Cyanobacterial Blooms (HCBs) represent one of the most conspicuous hazards to human health in freshwater ecosystems, due to the uses of the water for drinking, recreation and aquaculture. Cyanobacteria are one of the main biological components in freshwater ecosystems and they may proliferate in nutrients rich ecosystems causing severe impacts at different levels. Therefore, several methods have been applied to control cyanobacterial proliferation, including physical, chemical and biological strategies. However, the application of those methods is generally not very efficient. Research on an eco-friendly alternative leading to the isolation of new bioactive compounds with strong impacts against harmful cyanobacteria is a need in the field of water environment protection. Thus, this paper aims to give an overview of harmful cyanobacterial blooms and reviews the state of the art of studying the activities of biological compounds obtained from plants, seaweeds and microorganisms in the cyanobacterial bloom control.

Keywords Harmful algal blooms · Cyanobacteria · Control · Biological compounds

Introduction

Eutrophication results from an excessive load of nutritive elements in the water (nitrogen and/or phosphorus) (Bhagowati and Ahammad 2018; Le Moal et al. 2019; Vinçon-leite and Casenave 2019) causing the increase of Harmful Cyanobacterial Blooms (HCBs). HCBs have numerous impacts on drinking water, irrigation, recreational activities, depleting oxygen, food web resilience, and ecosystem integrity, and contribute to the lethality of some species (fishes and aquatic invertebrates) (Carmichael and Boyer 2016; Aguilera et al. 2018; Janssen 2019; Jia et al. 2019). Moreover, many cyanobacteria are known as toxin producers that can have harmful consequences on aquatic fauna and flora as well as the health of land plants, animals and humans (Bownik 2016; Huisman et al. 2018; Paerl 2018; Saraf et al. 2018). Toxic cyanobacteria blooms can also lead to economic losses related to blooms mitigation and lake restoration (Díaz et al. 2019;
Smith et al. 2019). The development and metabolism of agricultural seeds and plants are affected by the use of contaminated water by cyanotoxins in irrigation (El Khaliloufi et al. 2016; Redouane et al. 2019). Taken this into account, the control of cyanobacterial blooms is fundamental to decrease the impacts. Various physical, chemical, and biological technologies have been proposed and used to control or mitigate microalgae in water systems (Park et al. 2017; Sun et al. 2018a; Zohdi and Abbaspour 2019). Their evident drawbacks, e.g. nonselective toxicity too many aquatic organisms, high cost and low efficiency, have restricted their application (Moreira et al. 2014; Scholz et al. 2017; Tan et al. 2019). Therefore, the use of new alternative methods with high efficiency, safety and economy for controlling HCBs, has become very important and urgent. In recent years, biological compounds isolated from many aquatic, terrestrial plants and microorganisms have received much more attention as alternatives to chemical agents (Zerrifi et al. 2018). This paper raises awareness for the environmental control methods of cyanobacterial blooms. Additionally, updated data regarding available plants, seaweeds and microorganisms compounds endowed with high properties to control cyanobacteria blooms are provided and critically discussed.

**General characteristics of HCBs**

Cyanobacteria are among the first oxygen-producing Gram-negative bacteria on our planet, with fossil remains dating over 3 billion years (Schopf 2002). They are a diverse group with more than 2000 species divided into 150 genera widespread in various ecosystems such as fresh, brackish and marine waters, hyper-saline habitats, rocks, ice and deserts (Hoffmann et al. 2005; Seckbach Seckbach, 2007; Whitton and Potts 2012; Lahrouni et al. 2015). In aquatic ecosystems, diverse genera of cyanobacteria are present, such as *Microcystis, Dolichospermum, Planktothrix, Lyngbya* and *Cylindrospermopsis* (Douma et al. 2010; Komarek 2015). They occur regularly in lakes (Gkelis et al. 2014; Sukenik et al. 2015; Moura et al. 2018) and drinking water reservoirs (Cheung et al. 2013; Grabowska and Mazur-Marzec 2014; Jančula et al. 2014; He et al. 2016; Hammou et al. 2018) with a population density varying from very small numbers to more than 10⁶ organisms/mL (Falconer and Humpage 2005). The distribution and development of cyanobacteria are affected by many factors. Anthropogenic eutrophication and climate change are considered the main factors promoting the proliferation and expansion of cyanobacterial blooms (O’Neil et al. 2012; Paerl and Paul 2012; Schindler 2012; Verspagen et al. 2014; Heisler et al. 2017; Mantzouki et al. 2018; Le Moal et al. 2019). Over 100 species of cyanobacteria are evaluated as toxic organisms due to the biosynthesis of cyanotoxins (Jayatissa et al. 2006). Among these genera, *Microcystis* is the most reported toxic bloom-forming, namely in Moroccan reservoirs (Loudiki et al. 2002; Oudra et al. 2002; Douma et al. 2010, 2017) as well as in lakes in Mexico (Vasconcelos et al. 2010) or reservoirs or water treatments plants in Portugal (Vasconcelos et al. 1993; Vasconcelos and Pereira 2001). According to their mode of action, cyanotoxins are grouped into four main types: neurotoxins, hepatotoxins, cytotoxins, and irritant or gastrointestinal toxins (Saker et al. 2007; Pearson and Neillan 2008; Bouaïcha and Corbel 2016). Of the recognized cyanotoxins, there are hepatotoxins among which microcystins are the most ubiquitous worldwide and deleterious (Niedermeyer et al. 2014). Microcystin (MCs) are a diverse family of cyclic heptapeptides with more than 270 variants that differ in amino acid composition and toxicity (Meriluoto et al. 2017; Spoof and Catherine 2017; Bouaïcha and Corbel 2019; Janssen 2019). MCs are potent hepatotoxins in that they act as specific inhibitors of protein phosphatases (PPs) (Gácsi et al. 2009) affecting multiple processes such as cell division, secretion, membrane transport and gene transcription and translation (Puddick et al. 2014). As soon as they proliferate excessively in the environment, cyanobacteria affect directly and indirectly the entire ecosystem. Generated cyanotoxins can cause mortality and other adverse effects in aquatic animals and invertebrates (Esterhuizen-londt et al. 2016; Zohdi and Abbaspour 2019). They can lead to water quality degradation, contamination of drinking water and sub-chronic or chronic health effects (Drobac et al. 2013; Kamal and Ahmad 2014). Other organic compounds, geosmin and 2-methylisoborneol, produced by some cyanobacterial genera *Dolichospermum, Aphanizomenon, Microcystis* and *Oscillatoria* imparts an earthy taste and odor to water with potentially significant economic losses in the fish farming’s (Bláha et al. 2004; Graham et al. 2010). Proliferation of cyanobacteria reduce the transparency and penetration of light into the aquatic ecosystem, which limits the growth of primary benthic producers (Abrantes et al. 2006), consequently a perturbation of food webs occur (Zingone and Enevoldsen 2000). Therefore, the control of cyanobacterial blooms is important and urgently required. Several strategies have been suggested to remove or suppress cyanobacterial blooms including chemical, physical, mechanical and biological methods (Mohamed et al. 2014; Sun et al. 2016b). In the case of physical and mechanical methods, harmful algae are controlled with ultrasound techniques (Park et al. 2017), artificial mixing (Visser et al. 2016), membrane filtration technology (Zhao et al. 2017a, b, 2018), ultraviolet (Rastogi et al. 2014; Pathak et al. 2019) and adsorption (Marzbali et al. 2017). These approaches are hindered by obvious disadvantages including high costs, energy intensive and low efficiency (Gao and Xie 2011). Chemical methods generally refer to the control of HABs with a range of chemical compounds such as metals (Magdaleno et al. 2013; Huh and Ahn
photosensitisers (Pohl et al. 2015), herbicides (Nagai et al. 2016) and other chemicals molecules. Their application in aquatic environment is not recommended due to their environmental persistence, non-target toxicity to aquatic organisms and humans, and the ability of affected populations to develop resistance to these compounds (Huisman et al. 2018). This has led to the development of more promising and environment friendly alternative approaches such as biological methods (Backer et al. 2015; Harke et al. 2016). The introduction of new grazers and competitors of cyanobacteria, such as mussel (White and Sarnelle 2014; Waajen et al. 2016), herbivorous fishes (Søndergaard et al. 2017), zooplankton (Montemezzani et al. 2017), microorganisms (bacteriophages, pathogenic bacteria or fungi) (Gerphagnon et al. 2015; Wichelen et al. 2016; Coloma et al. 2017) and macrophyte (Liu et al. 2018), were used as the most popular biomanipulation. Nevertheless, the introduction of new species in an environment can lead to an alteration of the entire food web (Zerrifi et al. 2018). Lately, natural compounds isolated from many organisms such seaweeds, plants and microorganisms have been considered as potential synthetic algicidal agents.

### Natural biological compounds potentially used for cyanobacterial blooms control

#### Seaweeds bioactive compounds

Seaweeds are currently being explored as novel and sustainable sources of bioactive compounds including alkaloids, fatty acids, flavonoids, polyphenols, polysaccharides, peptides, sterols, proteins and other bioactive compounds (Wang et al. 2018a). Several studies have been focusing on exploring the chemical components and functions of seaweeds that can hamper the spread of microalgae or even eliminate them (Table 1). Zerrifi et al. (2018) studied the effect of the green macroalgae *Codium elongatum* methanolic extract on the growth of the filamentous cyanobacterium *Phormidium* sp. and reported that the growth of the tested microalgae has been strongly inhibited by the *C. elongatum* methanolic extract. Furthermore, Zerrifi et al. (2019) screened 14 species of Moroccan seaweeds and assessed their activity against the growth of the toxic cyanobacteria, *Microcystis aeruginosa*. On one hand, the methanolic extracts of the red macroalgae *Bornetia secundiflora* showed the most

| Table 1 Principal anti-microalgal compounds isolated from seaweeds | Seaweeds species | Chemical compounds | Target species | References |
| --- | --- | --- | --- | --- |
| *Iishige sinicola* | Octadeca-6Z,9Z,12Z,15Z-tetraenoic acid (ODTA), arachidonic acid and 1-O-palmitoyl-3-O-(6-sulfo-alpha-n-quino-vopyranosyl)-sn-glycerol | *H. akashiwo* and *Alexandrium catenella* | Hirao et al. (2012) |
| *Ulva intestinalis* | (6E,9E,12E)-(2-acetoxy-β-D-glucose)-octadecatrienoic acid ester | *H. akashiwo* and *P. mican* | Sun et al. (2016a) |
| *Ulva pertusa* | 8-Hexadecenol, 3,7,11,15-Tetramethyl-2-hexadecen-1-ol | *A. carterae* and *H. akashiwo* | Sun et al. (2018c) |
| *Gracilaria lemaneiformis* | 7,10-Epoxy-ar-bisabol-11-ol | *H. akashiwo* | Sun et al. (2017) |
| *Ulva fasciata* | Glycerol monopalmitate | *A. carterae*, *H. akashiwo*, *Phaeocystis globosa*, *P. donghaiense* and *S. costatum* | *H. akashiwo*, *P. globosa* and *P. donghaiense* | Alamsjah et al. (2005) |
| *Ulva prolifera* | Hexadeca-4,7,10,13-tetraenoic acid (HDTA) | *H. akashiwo* | Alamsjah et al. (2005) |
| *Porphyra yezoensis* | Gossonorol | *H. akashiwo*, *K. mikimitoi*, *P. globosa*, *P. donghaiense* and *S. costatum* | Sun et al. (2018b) |
| *Gracilaria lemaneiformis* | 7,10-Epoxy-ar-bisabol-11-ol | *H. akashiwo* and *K. mikimitoi* | Sun et al. (2018b) |
| *Corallina pilulifera* | 5,8,11,14,17-Eicosapentaenoic acid (EPA) | *Cochlodinium polykrikoides* | Oh et al. (2010) |
imported activity on solid medium with growth inhibition zone higher than 27 mm. On the other hand, the maximum inhibition rates were generated by *Bifurcaria taberculata*, *C. elongatum*, and *B. secundiflora* extracts in liquid medium (Zerrfi et al. 2019). Similarly Shi et al. (2018a), showed that the growth of *Chlorella vulgaris* and *Scenedesmus sp.* was strongly inhibited by *Ascophyllum nodosum* acetone extract (over 80%). They suggested that the mechanism of microalgal control could be related to the interaction between the extract and the antioxidant defense since the superoxide dismutase (SOD) and catalase (CAT) activities were very significantly depressed by high concentrations of the extract. Moreover, Jin et al. (2007) investigated the toxic effect of the green algae *Ulva pertusa* and *Ulva linza* extracts on *Prorocentrum micans* with strong growth inhibition. The minimum inhibitory concentrations values of crude extracts of *Ulva lactuca* and *Laurencia johnstonii* against some species of temperate marine microalgae such as *Halamphora coffeiformi*, *Cylindrotheca closterium*, *Navicula jeffreyae*, *Pleurochrysis roscoffensis*, *Exanthemachrysi gayraliae* and *Chlorarachniion globosum* ranged between 10 and 25 μg/mL (Águila-Noemí et al. 2012). Li et al. (2018) reported that an ethanol extract and isolated fraction of *Laminaria “sanhai”* showed significant algicidal effect against *Skeletonema costatum* (EC50 and LC50 values were 8.9 and 7.4 μg/mL, respectively). The GC–MS profile of the isolated bioactive substances demonstrated the abundance of fatty acids containing myristic, hexadecanoic, oleic, linolenic, arachidonic and eicosapentaenoic acids.

Recently, nine compounds were successfully isolated from green algae *U. pertusa* as trehalose (1), twenty-two methyl carbonate (2), (−)-dihydromenisdaurilide (3), 3,7,11,15-tetramethyl-2-hexadecen-1-ol (4), isophytol (5), 8-hexadecenol (6), 17-hydroxyheptadecanoic acid (7), trans-asarone (8) and 2-amino-3 mercaptopropanoic acid (9). The compound 6 displayed the most potent algicidal activity against *Amphidinium carterae* and *Heterosigma akashiwo*, whereas the compound 4 showed the strongest activity against *Karenia mikimitoi* and *Phaeocystis globosa* (Sun et al. 2018c). Also, the antialgal activity of α-linolenic acid (ALA) that is generally extracted from diverse macroalgae such as *Sargassum thunbergii* and *Corallina pilulifera* was assessed against *Prorocentrum donghaiense*. The results showed that ALA significantly inhibited the growth of *P. donghaiense*. Besides, the cellular morphology and ultrastructure of the tested microalgae were damaged (Wang et al. 2018b). After isolation of three compounds from *Ulva prolifera* such as 1-O-palmitoyl-3-O-β-D-galactopyranosyl glycerol (1), 1-O-oleadecanoic acid-3-O-β-D-galactopyranosyl glycerol (2), and 1-O-palmitoyl-2-O-oleoyl-3-O-β-D-galactopyranosyl glycerol (3). Their algicidal activity revealed that compound 2 showed the strongest activity (Sun et al. 2019).

### Natural substances from plants

Aquatic and terrestrial plants produce a high range of bioactive compounds that may have many biological functions. Several of these bioactive compounds can affect the growth and development of toxic microalgae (Mohamed 2017; Nguyen and Tran 2019) (Table 2). Zhang et al. (2014) showed that the growth of the toxic cyanobacteria *M. aeruginosa* was strongly inhibited using ginkgolic acids extracted from *Ginkgo biloba*. They also reported that ginkgolic acids cause morphologic damage or lysis of cells by decreasing total antioxidant and superoxide dismutase activities and increasing malondialdehyde content. Besides, these acids inhibited the transcription of three photosynthetic genes, namely *psaB*, *psbD*, and *rbcL* and two nutrient uptake related genes: *nca* and *phoU*. According to the same authors, these acids also affect the microcystin contents and the transcription of microcystin-related genes. Recently, Xu et al. (2019) studied the effect of *Spartina alterniflora* on the growth of *P. globosa* and *P. donghaiense*. The *S. alterniflora* ethanolic extract showed significant anti-algal activity against both microalgae tests at high concentrations but differed in their sensitivities (*P. donghaiense* was less sensitive than *P. globosa*). They revealed also that the extracts of *S. alterniflora* have reduced the photosynthetic efficiency and the relative maximum electron transport rate of both microalgae tests; therefore, implying a perturbation of the microalgae photosynthetic systems. On one hand, the exposure of *M. aeruginosa* to *Eichhornia crassipes* induced cell death. On the other hand, the photosystem (PS) II-Hill reaction in *M. aeruginosa* was not interrupted by *E. crassipes*, but a positive relationship between algal biomass and phyto cyanin was revealed (Zhou et al. 2014). Chen et al. (2018) investigated the anti-cyanobacterial activity of *Cinnamomum camphora* fresh leaves extracts prepared by methanol and water against *M. aeruginosa* and *Chlamydomonas reinhardtii*. The highest activity was obtained with the methanolic extract against both microalgae tests. The results of the GC–MS analysis of the tested extracts revealed the presence of 23 and 32 compounds in the water and methanolic extracts, respectively; camphor, α-terpineol and linalool were the three main compounds. Newly, the water extract of *Enhalus acoroides* showed significant growth inhibition of *P. globosa*. After Ultraperformance Liquid Chromatography-High Resolution Mass Spectrometry (UPLC-HRMS) analysis, six of twelve chemical constituents were flavonoids, with the predominance of luteolin-7-O-glucide. In another study, Zhu et al. (2019) proved that this major compound was one of the antialgal compounds of *E. acoroides* aqueous extract. Pakdel et al. (2013) demonstrated that the extracts, exudates and live material of *Chara australis* act as growth inhibitor of *Dolichospermum variabilis*, with no biological toxicity against the green alga *Scenedesmus quadricauda.*
| Plants species          | Compound/fraction used or solvent | Target species       | Effects                                                                 | References          |
|------------------------|----------------------------------|----------------------|----------------------------------------------------------------------|---------------------|
| *Artemisia annua*      | Artemisinin                      | *M. aeruginosa*      | Growth inhibition of *M. aeruginosa*, reduction of protein content and increase of superoxide dismutase activity and ascorbic acid content of *M. aeruginosa* | Ni et al. (2012)    |
| *Sagittaria trifolia*  | Aqueous extract                   | *M. aeruginosa*      | Inhibitory effect on the growth, the activities of superoxide dismutase and peroxidase and the glutathione content of *M. Aeruginosa* | Li et al. (2016)    |
| *Oryza sativa* (Rice straw) | Aqueous extract              | *M. aeruginosa*      | Suppression of algal cell growth in a concentration-dependent way       | Hua et al. (2018)   |
| *Cinnamomum camphora* | Camphor, α-terpineol and linalool | *M. aeruginosa* and *C. reinhardtii* | Individual compounds and their mixture reduced significantly the growth of both tested microalgae by inducing photosynthetic pigment degradation and declining PSII efficiency | Chen et al. (2018) |
| *Acorus calamus*       | Ethanol extract                   | *M. aeruginosa*      | The total algal biomass and chlorophyll a concentration decreased more than 90% after 7 days of treatment | Zhang et al. (2016b) |
| *Ailanthus altissima*  | Ethyl alcohol extract             | *M. aeruginosa*      | Inhibition of *M. aeruginosa* cells density, decrease in the amount of extracellular cyanotoxin microcystins and destruction of cells photosynthetic structure | Meng et al. (2015)  |
| *Ranunculus aquatilis* and *Nasturtium officinale* | Aqueous extract | *M. aeruginosa*      | *R. aquatilis* had the highest inhibitory effect on Microcystis growth | Tazart et al. (2019) |
| *Achillea ageratum* and *Origanum compactum* | Aqueous extract | *M. aeruginosa*      | Both extracts inhibit *M. aeruginosa* growth in a concentration-dependent way | Tebaa et al. (2017) |
| *Thymus satureioides* and *Artemisia herba alba* | Aqueous extract | *M. aeruginosa*      | The extract *T. satureioides* was more effective than *A. herba alba* for *M. aeruginosa* controlling | Tebaa et al. (2018) |
| *Eupatorium fortune*   | 2-Hydroxy-cinnamic acid           | *M. aeruginosa* and *C. vulgaris* | The compound was more toxic to *M. aeruginosa* than *C. vulgaris* at all tested concentrations | Nga et al. (2018)   |
| *Ceratophyllum demersum*, *Eichhornia crassipes*, *Polygonum tomentoseum* and *Saccharum spontaneum* | Acetone, methanol, ethanol and chloroform extracts | *M. aeruginosa*      | *E. crassipes* ethanolic extract exerted the most powerful inhibition | El-sheekh et al. (2017) |
| *Eleocharis dulcis*    | 3′,4′,5,7-Tetrahydroxyflavanone  | *M. aeruginosa*      | Oxidative damage of *M. aeruginosa* cells                             | Wen et al. (2018)   |
| Plants species | Compound/fraction used or solvent | Target species | Effects | References |
|----------------|----------------------------------|----------------|---------|------------|
| Acorus calamus, Oenanthe javanica and Sagittaria sagittifolia | Mixture of hexane, ethyl acetate and ethanol | M. aeruginosa, Dolichospermum flos-aquae and Aphanizomenon flos-aquae | M. aeruginosa was only sensitive to A. calamus and O. javanica extracts, while A. flos-aquae and Aphanizomenon flos-aquae was sensitive to the three macrophytes extracts | Zhang et al. (2015b) |
| Potamogeton crispus and Myriophyllum spicatum | Petroleum ether, methylene chloride, chloroform, acetone and methanol extracts | Pseudokirchneriella subcapitata | Chloroform extract and mixed extracts of the two plant showed the highest antialgal potential with P. subcapitata | Haroon and Abdel-aal (2017) |
| Portulaca oleracea | Acetone extract | M. aeruginosa | The inhibitory rate was more than 80% | Wang et al. (2017) |
| Dracontomelon duperreanum | Osmosis water extract | M. aeruginosa | Suppression of M. aeruginosa growth | Wang et al. (2018c) |
| Vallisneria spiralis | p-Coumaric acid and vanillic acid | M. aeruginosa | Growth inhibition of M. aeruginosa, activation of superoxide anion radicals generation in M. aeruginosa cells | Zhang et al. (2010) |
| Myriopyllum spicatum | Pyrogallic acid and gallic acid | M. aeruginosa | Reduction of photosynthetic activity of M. aeruginosa by inhibiting the activity of PSII | Zhu et al. (2010) |
| Eichhornia crassipes | N-phenyl-2-naphthylamine | S. quadricauda and M. aeruginosa | The green algae S. quadricauda was sensitive than the cyanobacteria M. aeruginosa | Pei et al. (2018) |
| Bidens pilosa | Ethanolic and methanolic extracts | M. aeruginosa | Inhibition efficiency in terms of the cell density and chlorophyll a concentration | Nguyen and Tran (2019) |
| Eichhornia crassipes | Aqueous extract | M. aeruginosa | Reduction of algae chlorophyll, superoxide dismutases, total protein contents in M. aeruginosa cells | Wu et al. (2019) |
Furthermore, the essential oils (EOs) as complex mixtures of components that can be divided into two groups: (i) terpene compounds and (ii) aroma compounds with an abundance of terpenes and their oxygenated derivatives, terpenoids; may possess a wide range of biological activities, including anti-microbial, antimicrobial and antioxidant activities (Raut and Karuppayil 2014; Jamali 2018). Nevertheless, the exploitation of EOs as a source for the discovery of new bioactive compounds with anti-microalgal properties is currently at an early stage. Very few studies have reported the anti-microalgal activities of EOs. Thus, after screening six emergent macrophytes EOs for their anti-cyanobacterial activity, Wang et al. (2015) showed that the growth of M. aeruginosa was inhibited by EOs of all tested macrophytes such as Potamogeton crispatus, Potamogeton maackianus, Potamogeton lucens, Vallisneria spinulosa, Ceratophyllum demersum and Hydrilla verticillata with inhibition rates being 35.1%, 36.2%, 32.9%, 41.7%, 30.2%, and 36.6%, respectively. The GC–MS identification of these EOs composition revealed the presence of fatty acids, ester, sterol, ketone and other compounds. Barani et al. (2015) reviewed the algicidal activity of three plants Satureja khuzistanica, Satureja rechingeri, and Zataria multiflora EOs on the dinoflagellate C. polykrikoides. They found that the highest algicidal activity was obtained by Z. multiflora EO (LC 50 equal to 1.35 µg/mL) with an abundance of carvacrol, thymol, and p-cymene. In that line, Najem and Abed (2018) investigated the effect of EOs excreted from Rosmarinus officinalis on M. aeruginosa and Chroococcus minor. The results demonstrated that the growth rates of both algae severely decreased as time increased and in a concentration-dependent way. Callicarpa americana EO recorded a complete growth inhibition when the treatment concentration was equal to 28.5 µg/mL (Tellez et al. 2000). Additionally, Wang et al. (2014) revealed the anti-cyanobacterial activities of two emergent plants Typha latifolia and Arundo donax. They reported that the inhibition rates increased by more than 40% against M. aeruginosa at 50.0 mg/L. The inhibitory activity of volatile compounds contained in two submerged macrophytes, C. demersum and Vallisneria spiralis on M. aeruginosa was studied by Xian et al. (2006). They found that the EO from C. demersum, composed of fatty acid compounds, terpenoids and phenolic compounds, showed stronger algicidal activity. Recently, Zerrifi et al. (2020) evaluated qualitatively and quantitatively the potential algicidal activity of Moroccan plants EOs. Qualitatively, the Chenopodium ambrosioides, Thymus broussonetii, Thymus maroccanus and Thymus satureioiides EOs inhibited the growth of M. aeruginosa, whereas Thymus palillus EO exhibited the weakest activity. Quantitatively, T. broussonetii EO displayed the greatest effectiveness (MIC = 0.047 mg/L and MBC = 0.095 mg/L). The weakest potency was achieved by T. pallidus EO (MIC = 12.5 mg/L and MBC = 25 mg/L).

**Natural compounds from microorganisms**

Through their environmental friendliness and great potential, microorganisms have received increasing attention as biological method for the control of HABs (Sun et al. 2018a). Algicidal microorganisms are defined as microorganisms capable to eliminate or reduce the negative effects of HABs in natural water. Several algicidal microorganisms species have been isolated from different natural environments (Demuez et al. 2015; Li et al. 2015a; Cai et al. 2016; Su et al. 2016; Xuan et al. 2017; Shi et al. 2018b; Yu et al. 2018). The study of algicidal compounds isolated from microorganisms is relatively rare which may be attributed to the difficulties encountered during the enrichment, isolation, purification and process identification. The compounds mainly comprise proteins, pigments, fatty acid compounds, amino acids, antibiotics, alkaloids and peptides (Sun et al. 2018a). The amino acid 4-hydroxyphenethylamine (Fig. 1) extracted from Acinetobacter guillouiae inhibits M. aeruginosa growth and microcystin-related genes and subsequently decrease microcystin production (Yi et al. 2015). Zhao et al. (2014) revealed that the growth of S. costatum, P. donghaiense, P. globose, and H. akashiwo was significantly suppressed by amino acid compounds such as l-histidine, o-tirosine, N-acetylhistamine and urocanic acid produced by Bacillus sp. strain B1. Palmitoleic acid (fatty acid compound) produced by the marine Gram-negative bacteria Vibrio sp. BS02 recorded algicidal activity against Alexandrium tamarense (Li et al. 2014). Lu et al. (2016) found that the purified algae-lysing compound, in Thalassospira culture filtrate, had the same retention time and the same measured elemental composition as standard benzoic acid. They reported that purified compound and standard benzoic acid promoted K. mikimotoi cell disruption and induced K. mikimotoi cell content leakage. Similarly, the brown microalga S. costatum NIES-324 was very sensitive to the serine protease extracted from Pseudomonas A28 (Lee et al. 2000).

![Fig. 1 Structure of 4-hydroxyphenethylamine isolated from A. guillouiae (Yi et al. 2015)](image-url)
Moreover, a red pigment (Prodigiosin) produced by Hahella KA22 showed a high algicidal effect on P. donghaiense, P. globosa, and H. akashiwo (Zhang et al. 2017). Deinoxanthin produced by Deinococcus sp. Y35 had strong algicidal activities against A. tamarense (Li et al. 2015b). Harmane (1-methyl-carboline) (Fig. 2) as alkaloid compound was isolated successfully from Pseudomonas sp. K44-1 ethyl acetate extract. Harmane showed antagonistic activities against several cyanobacterial strains such as M. aeruginosa and Microcystis viridis, at a concentration of 30 µg/disk (Kodani et al. 2002). Alamri and Mohamed (2013) also investigated the activity of two b-carbolines compounds (harmine, norharmane) produced by Bacillus flexus strain EMGA5 toward some cyanobacteria i.e. Merismopedia tenuissima, Oscillatoria limnetica and green microalgae (C. vulgaris and Ankistrodesmus falcatus). They found that both compounds were cytotoxic against the cyanobacterial test organisms (harmine was more toxic than norharmane). While the b-carbolines compounds have no toxicity against feed microalgae. Jeong et al. (2003) demonstrated that Bacillus sp. secreted a polypeptide, named Bacillamide, endowed with a specific algicidal effect on C. polykrikoides.

Some fungi also can produce algicidal compounds. Two new active polyketide metabolites named cis-4-acetoxyoxymellein and 8-deoxy-6-hydroxy-cis-4-acetoxyoxymellein (Fig. 3) purified from Meliotus dentatus endophytic fungus, an unidentified ascomycete, displayed good algicidal activity against Chlorella fusca (Hussain et al. 2015). (−)-phyllostine isolated from an endophytic fungus, Phomopsis sp., from Notobasis syriaca showed good algicidal property against C. fusca (Hussain et al. 2011). Also, the cycloepoxytriol B extracted from the ethyl acetate soluble fraction of Phomopsis sp. recorded a great activity against the green microalga C. fusca (Hussain et al. 2009).

Besides, researches on compounds purified from actinomycetes are relatively limited Zhang et al. (2016a) studied the effect of indole derivatives; tryptamine and tryptoline; isolated from Streptomyces juijangensis JXJ-0074 T showed higher antialgal activity against M. aeruginosa, Nostoc punctiforme, and Oscillatoria tenuissis by damaging cyanobacteria cells causing crumpling, perforation, breakage of filamentous cyanobacteria, decrease of the chlorophyll and superoxide dismutases and increases in superoxide anion radical (O$_2^−$) and malondialdehyde (MDA) content against C. fusca (Zhang et al. 2015a). Zheng et al. (2012) revealed that NIG355 compound, purified and identified from the marine actinomycete Streptomyces malaysiensis O4-6, shows high algicidal activity against P. globosa.

**Research critical views**

Faced with the problem of the massive proliferation of blooms around the world causing major public health issues because of their toxicities, the search for environmentally friendly solutions to curb this scourge must be well documented (Cai et al. 2016). Without strict attention, the so-called solution could cause enormous damage (Ye et al. 2020). To date, laboratory experiments are mostly proposed to control the emergence of HABs, using biological products extracted from microorganisms, both terrestrial and aquatic plants. At this stage, several studies have shown the efficacy of the algicidal properties of various

![Fig. 2 Structure of harmane extracted from Pseudomonas sp. (Kodani et al. 2002)](image)

![Fig. 3 Structure of cis-4-acetoxyoxymellein (1) and 8-deoxy-6-hydroxy-cis-4-acetoxyoxymellein (2) isolated from M. dentatus (Hussain et al. 2015)](image)

![Fig. 4 Chemical structure of indole derivatives purified from S. eurocidicus (Zhang et al. 2016a)](image)
biological extracts (Hua et al. 2018; Nguyen and Tran 2019; Tazart et al. 2019; Wu et al. 2019). Indeed, these extracts, aqueous or with organic solvents i.e. methanol, ethanol, or ethyl acetate are so effective that they could inhibit the growth of several species simultaneously (Wang et al. 2010; Meng et al. 2015; Liu et al. 2018; Zerrifi et al. 2019). Thus, since these extracts are used to control the development of dominant species, the impact on minority species is often neglected. Several authors are reluctant to directly apply biological extracts on a large scale and recommend extensive studies (Cai et al. 2016; Ye et al. 2020). Nevertheless, other studies claim that the application of these natural products only kills the targeted toxic cyanobacteria while having no effect on other phytoplanktonic algae (Oh et al. 2010; Alamri and Mohamed 2013; Cai et al. 2016; Zhang et al. 2020). On the other hand, due to the scarcity of studies supporting the specific activity of extracts on HCBs, the authors often test on only a few species of green algae before confirming that the extracts act only on the target cyanobacteria. It would be more prudent to consider that in nature there are more species than those considered in some studies. Therefore, further experiments such as mesocosm trials should be conducted to undoubt edly prove that these natural products will actually be safe for aquatic ecosystems in general. In addition, most studies agree that these extracts or their purified derivatives act to increase the permeability of the plasma membrane and thus significantly disrupt the photosynthetic function of algae (Cai et al. 2016; Zhang et al. 2020) suggesting that other photosynthetic organisms could be impeded. Thus, Liu et al. (2018) observed that four polyphenols extracted from M. spicatum, i.e., ellagic, gallic, pyrogallic acids and catechin acted synergistically to inhibit the growth of M. aeruginosa while simultaneously suppressing several other types of green algae.

Aqueous extracts are less effective compared to extracts with other organic solvents (El-sheekh et al. 2017; Haroon and Abdel-aal 2017). This is because aqueous extracts contain fewer compounds than those with organic solvents (Chen et al. 2018). Crude extracts are much more toxic to algae than their purified counterparts. This confirms the synergistic effect of the compounds in the extract (Jamali et al. 2017; Liu et al. 2018). Another aspect to consider would be the concentration of the extract to be applied and, therefore, the amount of extract that would be needed for a large scale application. An estimation by Meng et al. (2015) conducted on Hongze Lake showed that with a water volume of 3.04×10⁹ m³, 6.08×10⁵ tons of A. altissima extracts at a concentration of 200 mg/L would be required to overcome a Microcystis bloom with an abundance of 1.35×10⁶ cells/L. In short, extracts based on microorganisms, terrestrial/aquatic plants may significantly contribute to mitigating the damage caused by HABs. To this end, efforts in this area are necessary to assess and clarify to what extent the use of biological extracts or molecules will affect the environment.

Conclusion

HCBs in water bodies represent potent, emerging and increasing threat on freshwater resources across the world. Therefore, the control and protection of those finite water resources require our best attention. To this end, some methods employing chemical compounds are the most commonly used to control and mitigate the proliferation of cyanobacterial blooms. Despite their performances, these methods present several downsides, namely, their high-cost demands and non-selective toxicity both towards other environment organisms and possibly to human health. Nowadays, it is essential to minimize associated risks of those chemical compounds and compensate them with biological compounds. However, research on these biological compounds is still scarce. It is important to notice that some biological extracts have proven their potential to mitigate HCBs. That is the case, for instance of some seaweeds essential oils, the major compounds of essential oils extracted from different plants and seaweeds and biomolecules released from microorganisms. Therefore, purification and identification of new active natural biomolecules secreted by several organisms and their mode of action and mechanisms on HCBs are necessary to be focused on in order to propose bioactive molecules useful on a commercial scale and applicable in the environment without ecological damages and disturbances.

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