



The application of seaweeds in environmental biotechnology

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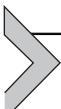
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Abstract

Apart from being applied as a source of human food, animal feed, fertilizers, components of cosmetics, pharmaceuticals and nutraceuticals, biofuels, fast-growing seaweeds can also be used to prevent environmental pollution, for bioremediation of polluted environment and in environmental biomonitoring (bioindication of marine ecosystem pollution). They are known to effectively remove toxic metals (e.g., arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, zinc) and organic compounds (e.g., DDT, PCB) from contaminated soil, industrial effluents and wastewater treatment. Biosorption of toxic metal ions by dry seaweeds is a kind of biotreatment of polluted water. Also the bioremediation of nutrients, generated by intensive aquaculture (e.g., fish, shrimps and other aquatic animals) in so-called integrated multitrophic aquaculture makes use of seaweeds. Macroalgae derived from unpolluted water – e.g., eutrophicated natural water reservoirs or remediated wastewater from aquaculture can be used for the production of components of fertilizers, feed additives and biochar which provides a multitude of benefits in terms of environmental management, e.g., climate change mitigation due to carbon sequestration, remediation of

contaminated sites (water, soil) due to very good sorption properties, plus the mitigation of contaminants movement in soil due to action as a landfill filter medium. The proposed biotechnological tools based on seaweeds biomass can improve the environment and assure its sustainability.



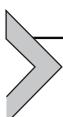
1. Introduction

According to the European Federation of Biotechnology, “Environmental biotechnology provides effective tools, which are sustainable from economic, environmental and social points of view and can be applied to: (1) monitor and reduce the risk to humans from contaminated sites and from the storage of municipal and industrial (bio)wastes, (2) clean up water, soil, and air to achieve good quality standards and reuse treated wastewater to reduce the demand of natural water for industrial, agricultural and municipal purposes and (3) turn (bio)waste, including wastewater, into bio-based biodegradable/biocompatible and renewable chemicals for material and fuel production” ([EFB, 2019](#); [Gavrilescu, 2010](#); [Wang, Ivanov, Tay, & Hung, 2010](#)).

In the present chapter, the possibilities of the seaweeds applications in the bioremediation of polluted water and soil and in the environmental monitoring are evaluated. Industrialization, urbanization, population growth and agriculture largely contribute to the degradation of the natural environment ([Bilal et al., 2018](#); [Chekroun & Baghour, 2013](#)). Humankind needs to remove from the environment toxic metals (e.g., arsenic, cadmium, mercury and lead) and organic compounds used in numerous industrial activities, such as: chemical, pigments, textile, plastics, storage batteries, electroplating, mining, smelting, metallurgical processes etc. ([Bilal et al., 2018](#); [Bulgariu & Bulgariu, 2017](#)). Heavy metals are especially dangerous because they are toxic, persistent in the environment, cannot be destroyed or degraded and tend to bioaccumulate in the food chain ([Arumugam et al., 2018](#); [Bulgariu & Bulgariu, 2017](#); [Ortiz-Calderon, Silva, & Vásquez, 2017](#); [Sati, Verma, Bora, & Rai, 2016](#); [van Ginneken & de Vries, 2018](#)). An important issue is also bioremediation of the contaminated soil with organic (e.g., pesticides, DDT (1,1,1-trichloro-2,2-bis (*p*-chlorophenyl) ethane), PCBs (polychlorinated biphenyls), PAHs (polycyclic aromatic hydrocarbons)) and toxic metals (e.g., As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn) ([Chekroun & Baghour, 2013](#); [Cheney, Rajic, Sly, Meric, & Sheahan, 2014](#); [Farias et al., 2017](#); [Kantachote et al., 2004](#)). Also eutrophicated water and effluents generated

by intensive aquaculture (farming of fish, shellfish, shrimp, sea urchin, abalone etc.) that are rich in biogens such as nitrogen and phosphorus pose a problem (Chopin, 2013; Neori et al., 2004). The effective removal of pollutants from industrial/aquaculture effluents and soil is one of the tasks of environmental biotechnology and conditions of sustainable development.

In order to reduce the level of contamination in water bodies and in soil, several remediation technologies have been implemented, for example the application of low-cost adsorbents in biosorption, chelating agents and biology-based techniques for example phytoremediation (Singh & Prasad, 2015). Seaweeds, also called marine macroalgae, which occur mainly in three phyla — brown (B; phylum Ochrophyta, class Phaeophyceae), green (G; phylum Chlorophyta) and red macroalgae (R; phylum Rhodophyta) — are promising candidates for the remediation technologies (Dawes, 2016). Macroalgae are of great ecological importance because they supply oxygen to seawater and constitute the most important element in the marine food chain — they are primary producers (Chan, Ho, & Phang, 2006). Seaweeds grow fast and abound in many regions all over the world, especially if the water is warm and acidified. An intensive seaweed proliferation is a symptom of eutrophication. Their biomass captures carbon and some nutrients like nitrogen and phosphorous (Arumugam et al., 2018; Bird, Wurster, Silva, Paul, & de Nys, 2012; Gao, Clare, Rose, & Caldwell, 2018; Seghetta, Torring, Bruhn, & Thomsen, 2016). The remediation technologies aiming at the reduction of water and soil contamination (and the same in the food chain) should render a great service in agriculture (Singh & Prasad, 2015). The examples of seaweeds applications in environmental biotechnology are presented in Fig. 1.



2. Bioremediation of toxic metal ions from wastewater

2.1 Biosorption by seaweeds

Bioremediation of toxic metals from wastewater by algae can be carried out through biosorption (using non-living organisms) or bio-accumulation (using living cells) (Aksu, 1998; Henriques et al., 2017). The former is known to be much faster and effective than the latter where higher concentrations of pollutants in wastewater can cause the death of living organisms (Aksu, 1998; Bilal et al., 2018). Therefore, biosorption, as a subcategory of adsorption is more often used for the removal of

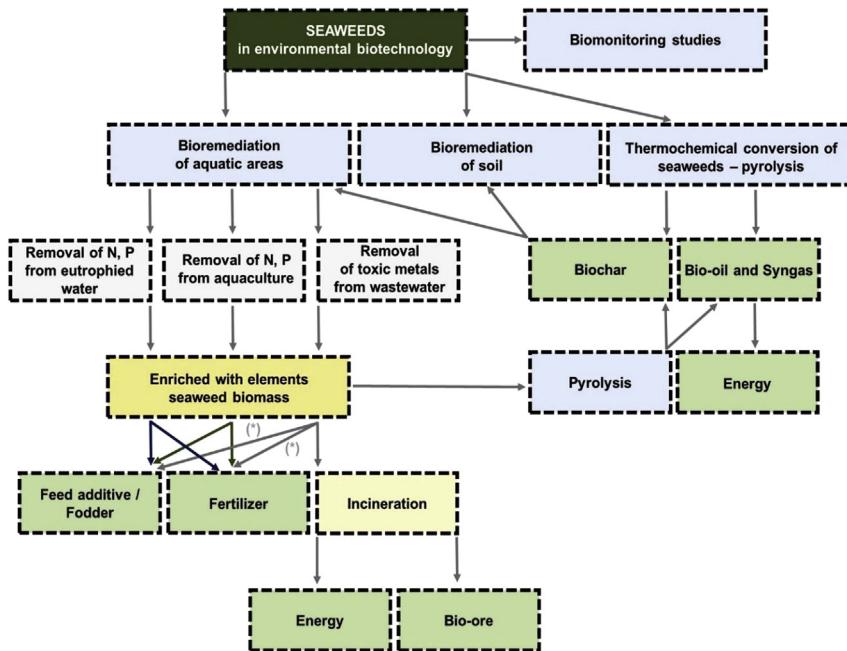


Fig. 1 The examples of seaweeds applications in the environmental biotechnology.

contaminants from wastewater than bioaccumulation. Biosorption is also recognized as one of the tools of environmental biotechnology ([Bulgariu & Bulgariu, 2017](#); [Deniz & Ersanli, 2018](#)). This process is used when other technologies such as chemical precipitation, coagulation, membrane separation, electrochemical reduction fail – incomplete metal removal especially when the concentration of metal ions is low and ranges from 1 to 100 mg/L or are too expensive ([Bilal et al., 2018](#); [Bordoloi, Goswami, Kumar, & Kataki, 2017](#); [Davis, Volesky, & Mucci, 2003](#); [Gadd, 2009](#); [Ortiz-Calderon et al., 2017](#); [Sati et al., 2016](#)).

Biosorbents of metal ions used in this process should be widely available, renewable, cost-effective and environment friendly ([Arumugam et al., 2018](#); [Bilal et al., 2018](#); [Bordoloi et al., 2017](#); [Bulgariu & Bulgariu, 2017](#); [Gadd, 2009](#); [Ortiz-Calderon et al., 2017](#)). Seaweeds have very good biosorption properties, which result from the presence of macromolecules (e.g., polysaccharides, proteins) in the algal cell wall which offer different functional groups such as amino, hydroxyl, carboxyl and sulfate, capable of binding metal ions ([Abd-Elhady & El-Zabalawy, 2014](#); [Bilal et al., 2018](#); [Davis](#)

et al., 2003; Sati et al., 2016). Macroalgae can efficiently remove different pollutants, such as dyes from paper, textile and printing industry, nitrogen, phosphorous and phenolic compounds (e.g., from aquaculture), and heavy metals from various sources (Arumugam et al., 2018; Vijayaraghavan & Ashokkumar, 2019). Ion exchange is indicated as a principal mechanism for biosorption of metal ions by dry macroalgal biomass – light metal ions from seawater such as calcium, magnesium, sodium, potassium naturally bound to the algal functional groups are exchanged with metal ions from wastewater (Bilal et al., 2018; Davis et al., 2003; Zeraatkar, Ahmadzadeh, Talebi, Moheimani, & McHenry, 2016).

Researchers still take an interest in this technique (Fig. 2): the total number of papers on biosorption by seaweed is 625 (according to the Web of Science database; July 12, 2019) within the timespan of 1900–2019. Key-words “biosorption by seaweed” was searched in the topic of papers.

Among all seaweed species, the most often examined in terms of biosorption are brown algae – 303 papers, then green algae – 131 papers and finally red algae – 61 papers (according to the Web of Science database; July 17, 2019). Search was done for keywords, for example “biosorption by green seaweed” in the topic of a paper. A similar analysis was performed for metal ions, which are the most often selected for biosorption by seaweeds. The total number of papers on biosorption of a given metal ion by seaweeds

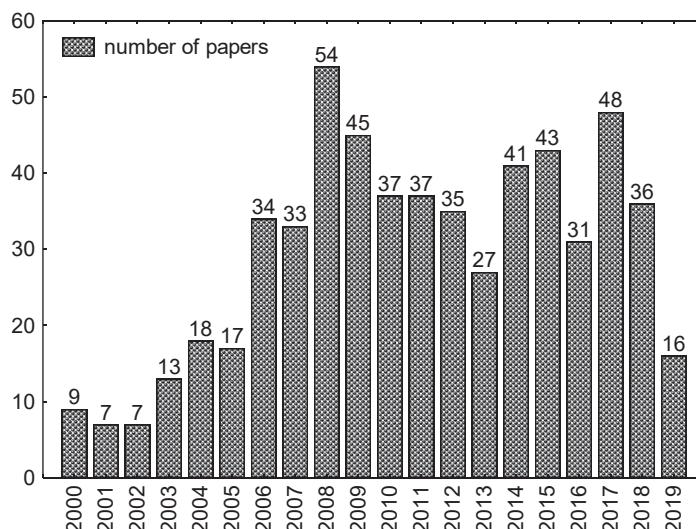


Fig. 2 Number of papers on biosorption by seaweed according to the Web of Science database (July 12, 2019).

is presented in Fig. 3. Keywords for example “biosorption of Cu by seaweed” were searched in the topic of papers (according to the Web of Science; July 12, 2019) for the timespan 1900–2019.

Effective removal of toxic metal ions from wastewater depends on many factors, such as biosorbent type (phylum) and size and the operating parameters of biosorption, such as initial solution pH, biosorbent dosage (C_S), initial metal ion concentration (C_0), temperature, contact time, single- or multi-metal system (the presence of competing ions), etc. These factors have all been described in detail (e.g., Bilal et al., 2018; Bulgariu & Bulgariu, 2017; Gadd, 2009; Sati et al., 2016; Zeraatkar et al., 2016). The examples of the removal of heavy metal ions such as Cd(II), Cu(II), Ni(II), Pb(II), Zn(II) by different seaweed species have been reported in many review papers or book chapters (Arumugam et al., 2018; Bilal et al., 2018; Bulgariu & Bulgariu, 2017; Chekroun & Baghour, 2013; Davis et al., 2003; Gadd, 2009; He & Chen, 2014; Michalak, Witek-Krowiak, Chojnacka, & Bhatnagar, 2015b; Ortiz-Calderon et al., 2017; Sati et al., 2016; Zeraatkar et al., 2016). The detailed biosorption performance of different algal-based biosorbents for the removal of heavy metals is presented by He and Chen (2014). The authors showed that brown algae are able to remove efficiently Pb(II) ions (with a biosorption capacity ranging from 166 to 284 mg/g), Cu(II) ions (from 50.8 to 105 mg/g), Cd(II) ions (from 59.6 to 131 mg/g), Zn(II) ions (from 32.7 to 59.5 mg/g), Ni(II) ions (from 5.3 to 62.8 mg/g), and Cr(III) ions (from 60.8 to 62.9 mg/g). In the case of green macroalgae, the biosorption capacity ranged from 26.9 to 302 mg/g for Pb(II) ions, from 5.1 to 114 mg/g for Cu(II) ions, from 4.5 to 88.8 mg/g

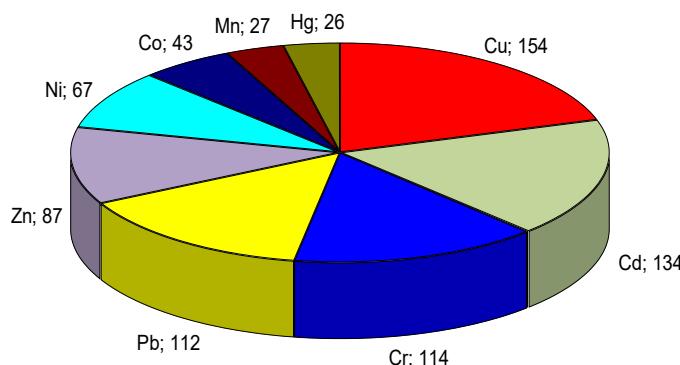


Fig. 3 Number of papers on biosorption of a given metal ion by seaweed according to the Web of Science (July 12, 2019).

for Cd(II) ions, from 2.6 to 35.3 mg/g for Zn(II) ions, from 12.9 to 66.9 mg/g for Ni(II) ions and from 36.9 to 53.0 mg/g for Cr(III) ions. For red seaweeds, these values were as follows: Pb(II) ions 29.0–203 mg/g, Cu(II) ions 21.0–40.0 mg/g, Cd(II) ions 16.9–85.4 mg/g, Zn(II) ions 21.6–45.1 mg/g, Ni(II) ions 16.4–37.0 mg/g, Cr(III) ions 28.1–105 mg/g, Co(II) ions 32.4–76.0 mg/g.

2.2 Biosorption by seaweed biochar

Waste algal biomass can itself be a biosorbent or can be transformed into another sorbent that is biochar. Biochar is known as a carbon-rich “biological charcoal” (Roberts, Cole, Paul, & de Nys, 2015a) and is produced during pyrolysis, a thermochemical conversion of the biomass (Bulgariu & Bulgariu, 2017; Michalak, 2018; Milledge, Smith, Dyer, & Harvey, 2014), which yields also bio-oil and syngas (Bird et al., 2012; Kim et al., 2016; Milledge et al., 2014) successfully used for energy production. Seaweed-derived energy is included in the category of “clean technologies” (Bulgariu & Bulgariu, 2017). Finding the application for biochar will enhance the economic feasibility of pyrolysis (Kim et al., 2016).

Seaweed biochar is used for sequestration of carbon in soil, soil amelioration, remediation of degraded soils, improvement of soil fertility (increase in the retention of nutrients and reduction of N₂O emissions from agricultural soils), as a source of bioenergy, and in the treatment of contaminated wastewater, etc. (Roberts, Paul, Dworjanyn, Bird, & de Nys, 2015b). Biochar produced from seaweeds, cultivated in unpolluted water does not contain excessive amounts of toxic elements that is why it can amend soil (Bird et al., 2012). All types of waste seaweed biomass, generated also by low temperature combustion or algae processing, for example oil or agar extraction can be used for the production of biochar rather than be disposed of in landfills or incinerated (Bulgariu & Bulgariu, 2017; Roberts et al., 2015d). Waste management after extraction of biologically active compounds from seaweeds will improve also the sustainability of macroalgae cultivation (Roberts et al., 2015d). Seaweed biochar can be suitable not only as a biosorbent of pollutants, but also in terms of resource recycling and energy efficiency (Poo et al., 2018). When waste is treated with waste, many contamination problems can find an effective solution (Roberts et al., 2015d).

The abundance of usually green seaweeds resulting from eutrophication (*Cladophora coelothrix*, *Cladophora patentiramea*, *Cladophora vagabunda*, *Chaetomorpha*, *Chaetomorpha linum*, *Cladophoropsis* sp., *Ulva flexuosa*) makes them

attractive as a source of biomass for biochar production (Bird, Wurster, de Paula Silva, Bass, & de Nys, 2011; Kim et al., 2016). Very popular are also seaweeds, which are not only abundant but also widely distributed such as *Undaria pinnatifida* (Cho et al., 2013), *Saccharina japonica* (Poo et al., 2018), *Sargassum fusiforme* (Poo et al., 2018) and *Gracilaria* sp. (Johansson, Paul, de Nys, & Roberts, 2016; Roberts et al., 2015d).

Seaweeds biochar is not as popular a biosorbent as seaweeds. Most of the papers describing biosorption properties of macroalgal biochar have been published in the recent few years (Table 1). Macroalgal biochar is rich in alkali and alkaline earth metals (calcium, magnesium, sodium and potassium), which originate from seawater (nutrients for the seaweed growth). These elements have a large exchangeable cation capacity, which enables the removal of heavy metal ions (Davis et al., 2003; Kim et al., 2016). Cho et al. (2013) and Kim et al. (2016) showed that steam activation could increase the surface area and the amount of cation exchange capacity of seaweed biochar. The temperature of pyrolysis can also influence the biosorption properties of biochar. Poo et al. (2018) demonstrated that *S. japonica* biochar obtained at temperatures higher than 400°C (among tested 250, 400, 500, 600 and 700°C), had removal efficiencies for Cd(II), Cu(II) and Zn(II) ions higher than 98%. For *S. fusiforme* biochar, the highest removal efficiencies (higher than 86%) for the same three heavy metal ions were obtained for seaweeds pyrolysis at temperatures over 500 °C.

Seaweed biochar can also remove oxyanionic elements such as As, Mo and Se as shown in the work of Kidgell, de Nys, Paul, and Roberts (2014) and Johansson et al. (2016). The authors used biochar and iron-biochar produced from *Oedogonium* sp. to remediate metals and metalloids from a coal-fired power station effluent. The biosorbent was shown to be more effective when the algal biomass was treated with a ferric solution before conversion to biochar through pyrolysis (Kidgell et al., 2014; Roberts et al., 2015d; Johansson et al., 2016). Biochar can be loaded with iron also after pyrolysis (Roberts et al., 2015d). Biosorption with iron-based sorbents is recognized as the most promising method for metalloid bioremediation (Kidgell et al., 2014; Roberts et al., 2015d; Johansson et al., 2016). Algal biochar may have better sorption properties than the alga itself. For example, Thivya and Vijayaraghavan (2019) demonstrated that biochar produced from *Kappaphycus alvarezii* exhibited dye sorption capacities 3.1 times higher than those of raw biomass. Algal biochar can be applied several times if washed with deionized water and dried (Song, Guo, Li, Zhao, & Yu, 2019). In the work of Vijayaraghavan and Ashokkumar (2019), low pH

Table 1 Removal of toxic metal ions and organic contaminants by seaweed biochar.

Seaweed	Sorbate	Experimental conditions	Maximum biosorption capacity (q_{\max}); mg/g	Reference
Inorganic – metal ions				
<i>Ulva compressa</i> (G); coast of Korea	Cu(II)	C_0 5–50 mg/L, C_S 0.1 g/L, 20 °C, 48 h, pH 5.5	^a 33 mg/g (biochar); 137 mg/g – biochar activated with water vapor stream, 20 mg/g – activated with KOH	Kim et al. (2016)
<i>Undaria pinnatifida</i> (B); southern coastal areas in Korea	Cu(II)	C_0 5–50 mg/L, C_S 0.1 g/L, 20 °C, 48 h, pH 5.0	^a 125.9 mg/g – biochar activated with water vapor stream	Cho et al. (2013)
<i>Saccharina japonica</i> and <i>Sargassum fusiforme</i> (B); Busan, Korea	Cu(II), Cd(II), Zn(II)	C_0 1500 mg/L, C_S 17 g/L, 20 °C, 24 h	Cu(II): <i>S. japonica</i> 98.6 mg/g (pyrolysis temp. 500 °C), <i>S. fusiforme</i> 94.1 mg/g (600 °C); Cd(II): both 700 °C – <i>S. japonica</i> 60.7 mg/g and <i>S. fusiforme</i> 37.2 mg/g; Zn(II): both 700 °C – <i>S. japonica</i> 84.3 mg/g and <i>S. fusiforme</i> 43.0 mg/g	Poo et al. (2018)
<i>Turbinaria turbinata</i> (B); Caribbean area, Guadeloupe	Cr(VI)	C_0 0–10 mg/L, pH 5.0, 25 °C	^a 12.6 mg/g – biochar activated with stream and 11.0 mg/g – activated with H_3PO_4	Yacou, Altenor, Carene, & Gaspard (2018)
<i>Gracilaria</i> sp. (R); (waste after agar extraction); Bogatama, Indonesia	Se, Mo, As	C_0 0.1 and 200 mg/L, C_S 10 g/L, 15 °C, 1 h	Mo 78.5 mg/g, As 62.5 mg/g and Se 14.9 mg/g	Johansson et al. (2016)

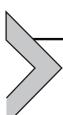
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Table 1 Removal of toxic metal ions and organic contaminants by seaweed biochar.—cont'd

Seaweed	Sorbate	Experimental conditions	Maximum biosorption capacity (q_{\max}); mg/g	Reference
<i>Gracilaria</i> sp. (R); (waste after agar extraction); Indonesia	Se(IV), Se(VI)	C_0 0.5 mg/L, C_S 10 g/L, pH 2.5, 4 and 8, 4 h, 20 °C	no effect of pH on biosorption: pH 2.5–2.60 mg/g; pH 4.0–2.72 mg/g; pH 8.0–2.66 mg/g	Roberts et al. (2015d)
<i>Hizikia fusiformis</i> (B); Jeju Island, Korea	Ni(II), Zn(II), Cu(II), Pb(II), Cd(II)	C_0 5–100 mg/L, C_S 1 g/L, pH 4, 25 ± 0.5 °C, 6 h	^a in a mixed solute system: Cu(II) 2.24 mg/g, Pb(II) 2.89 mg/g, Ni(II) 12.1 mg/g, Cd(II) 22.0 mg/g, Zn(II) 22.2 mg/g	Shin (2017)
Organic				
<i>Kappaphycus alvarezii</i> (R)	Reactive blue 4 (RB4), Reactive orange 16 (RO16)	C_0 50–500 mg/L, C_S 4 g/L	RB4 – 0.324 mmol/g, RO16 – 0.140 mmol/g	Thivya & Vijayaraghavan (2019)
<i>Sargassum</i> sp. (B); coast of Singapore	tetracycline; cefradine	C_0 20 mg/L, C_S 0.4 g/L, 24 h	^a tetracycline 128 mg/g; cefradine 61.7 mg/g	Song et al. (2019)
<i>Turbinaria conoides</i> (B); Mandapam region, a coastal area of Tamilnadu (India)	Remazol brilliant blue R (Reactive blue 19)	C_0 50–500 mg/L, C_S 4 g/L, pH 2, 32 °C, 8 h	^a 92.5 mg/g	Vijayaraghavan & Ashokkumar (2019)

^a— determined from Langmuir equation.

conditions were favorable for the biosorption of dye – Remazol brilliant blue R (Reactive blue 19) by biochar produced from brown seaweed *Turbinaria conoides*. Therefore, the elution of dye from loaded biochar was carried out by means of alkaline elutants (0.1 M Na₂CO₃ and 0.1 M NaOH). Table 1 presents examples of the removal of inorganic (toxic metal ions) and organic compounds (dye, antibiotic) by seaweed biochar. The results point to the conclusion that seaweed biochar is a prospective and effective adsorbent for wastewater treatment systems. Biochar produced from waste algal biomass is believed to be able to replace expensive commercial activated carbon (Kim et al., 2016).



3. Bioremediation of nutrients by seaweeds

3.1 Eutrophicated water

Marine eutrophication occurs in many places all over the world. The cultivation of seaweeds in coastal waters can be useful to alleviate eutrophication and to control harmful algae blooms that result in animal death and economic loss (Wu et al., 2015a; Xiao et al., 2017; Xu, Fang, & Wei, 2008; Yang et al., 2015; Zheng, Jin, Zhang, Wang, & Wu, 2019). The efficient cultivation of algae requires suitable environmental factors, such as light, appropriate temperature, content of nutrients, salinity, cultivation depth, water movement and the presence of epiphytes and herbivorous fish (Yang et al., 2015). During bioremediation of eutrophicated water, the nitrogen content in seaweed tissues increases with the increase in the concentrations of dissolved nitrogen in seawater (Chung, Kang, Yarish, Kraemer, & Lee, 2002). The production of seaweeds with a high tissue protein and carbohydrate content has the potential for biorefinery (Ashkenazi, Israel, & Abelson, 2019; Ross et al., 2018). The macroalgal biomass can be also sustainably returned to agricultural land or be used for the manufacture of valuable products, thus meeting both economic and ecological objectives. In this context, seaweeds aquaculture can be considered as “vegetables cultivation in the sea” with high nutritional value. When compared with terrestrial vegetable cultivation, farming of macroalgae in eutrophicated water saves the fertilizer, pesticides, and consequently farmland (Zheng et al., 2019). Other environmental benefits offered by seaweed aquaculture include carbon sequestration, CO₂ absorption, release of oxygen into coastal waters and iodine production (Yang et al., 2015; Zheng et al., 2019). The removal of nutrients from eutrophicated water through seaweeds cultivation

is the most popular in China where approximately 9500 tons of phosphorus and 75,000 tons of nitrogen is removed annually (Xiao et al., 2017). China's large-scale seaweed aquaculture accounts for over $\frac{2}{3}$ of the global production (Xiao et al., 2017; Zheng et al., 2019).

Green seaweeds *Ulva* sp. (Amosu, Robertson-Andersson, Kean, Maneveldt, & Cyster, 2016; Aníbal et al., 2014; Chung et al., 2002; Zheng et al., 2019), *Ulva clathrata* (Aníbal et al., 2014), *C. coelothrix* and *Cladophora parriaudii* (Ross et al., 2018); red seaweeds *Porphyra* sp. (Carmona, Kraemer, & Yarish, 2006; Chung et al., 2002; Wu et al., 2015a; Zheng et al., 2019) and *Gracilaria* sp. (Marinho-Soriano et al., 2011; Xu et al., 2008; Yang et al., 2015; Zheng et al., 2019; Zhou et al., 2006) are some of the most popular algal species used in the bioremediation of eutrophicated water. Green seaweeds, which abundantly occur in the marine environment and are characterized by a rapid growth rate and a broad spectrum of environmental tolerance, are the best candidates to sequester carbon, nitrogen and phosphorus (Aníbal et al., 2014; Bird et al., 2011; Lawton, Mata, de Nys, & Paul, 2013; Ross et al., 2018). *Ulva* and *Cladophora* are also responsible for seaweed blooms, called green tides around the world (Abd-Elhady, 2015; Abd-Elhady & El-Zabalawy, 2014; Cheney et al., 2014; Farias et al., 2017; Ross et al., 2018). Red algae can better be used in aquaculture than brown algae because they usually have higher average nitrogen content, mainly due to their photosynthetic pigments (N-containing phycobiliproteins) and protein levels (Carmona et al., 2006; Chung et al., 2002). Some red seaweed species (e.g., *Gracilaria* sp.) offer a high yield and additionally produce valuable compounds, for example agar-agar, a type of food for humans and fodder for animals (Zhou et al., 2006). Yang et al. (2015) indicated that *Gracilaria* in Chinese coastal waters remediates contaminants from aquaculture, sequesters carbon dioxide, mitigates eutrophication, and controls harmful algal blooms, thus maintaining healthy mariculture systems.

Wu et al. (2015a) showed that during the large-scale cultivation of *Porphyra yezoensis* in open sea in China (South Yellow Sea), mean nutrient concentrations in the cultivation area were significantly lower than in the non-cultivation one. Reduction efficiency of the nutrients in seawater was NH₄-N 44%, NO₃-N 49%, and PO₄-P 45%. Huo et al. (2011) showed that the nutrient removal by red seaweed *Gracilaria longissima* in Hangzhou Bay, Shanghai (East China Sea) was slightly higher (54% 75% 49%, respectively) than for *P. yezoensis* examined in the work of Wu et al. (2015a). Marinho-Soriano et al. (2011) indicated that in order to remove nutrients efficiently, macroalgae cultivation should be combined

with animal farming. The authors performed experiments consisting of three treatments: (1) macroalgae (*Gracilaria caudata*), (2) macroalgae and microcrustacean (*Artemia franciscana*) and (3) *Artemia* alone, with the best results being obtained for the second option (removal was NO₂ 100%; NO₃ 72.4%; NH₄ 29.8% and dissolved inorganic nitrogen 44.5%). Seaweed cultivation acting as a nutrient scrubber system can be one of the best reasons for bioremediation of coastal eutrophicated waters (Chung et al., 2002; Ross et al., 2018).

3.2 Aquaculture

Aquaculture, which covers the farming of both animals (including crustaceans, fish and molluscs) and plants (including seaweeds and freshwater macrophytes) can be practised in inland (freshwater) and coastal (brackish water, seawater) areas (Edwards & Demaine, 1997; Neori et al., 2004). Intensive aquaculture production requires a high input of water, fertilizers, feeds and other chemicals, which produces considerable amounts of wastes with all accompanying environmental problems (Chung et al., 2002; Neori et al., 2004; Zhou et al., 2006). Fish excretion and feces production induce eutrophication, harmful algal blooms, loss of biodiversity, anoxia in bottom waters and coastal-water pollution (Silva, Yáñez, Martín-Díaz, & DelValls, 2012; Yang et al., 2015; Zhou et al., 2006).

Integrated Multitrophic Aquaculture (IMTA) is a system in which effluents from aquaculture production are used as a nutrient for further production of animals and seaweed biomass. Here seaweeds can be used for wastewater bioremediation (as biological filters to remove inorganic nutrients) or/and as feed additives for aquaculture (fish, shrimp, molluscs etc.) (Arumugam et al., 2018; Ashkenazi et al., 2019; Bird et al., 2011; Elizondo-González, Quiroz-Guzmán, Escobedo-Fregoso, Magallón-Servín, & Peña-Rodríguez, 2018; Grote, 2016; Hou et al., 2012; Lamprianidou, Telfer, & Ross, 2015; Largo, Diola, & Marababol, 2016; Lavania-Baloo, Azman, Said, Ahmad, & Mohamad, 2014; Marinho-Soriano et al., 2011; Neori et al., 2004; Silva et al., 2012; Wei et al., 2017; Wu, Huo, Hu, Wei, & He, 2015b; Yang et al., 2015; Zhang, Hansen, Fang, Wang, & Jiang, 2009; Zhou et al., 2006). Oxygen produced by seaweed through photosynthesis can improve the respiration of cultivated animals (Neori et al., 2004; Yang et al., 2015) and provide them with a positive environment (Wei et al., 2017). Some seaweeds, for example *Gracilaria* sp., are able to inhibit the growth of phytoplankton including species such as *Prorocentrum donghaiense*, *Scrippsiella trochoidea*, *Alexandrium tamarensis*, *Dunaliella salina*, *Skeletonema*

costatum, *Heterosigma akashiwo* that cause harmful microalgal blooms (Yang et al., 2015).

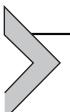
Decomposing animal waste produced by farms releases nutrients in abundance, which pollute the cultivation, and the surrounding waters (Yang et al., 2015). Total ammonia nitrogen (unionized ammonia; NH_3) and ionized ammonia (NH_4^+) are the main excretory products of fish nitrogen metabolism. Concentrations higher than 1.5 mg $\text{NH}_3\text{-N/L}$ can be toxic to most fish (Dosdat, Servais, Métailler, Huelvan, & Desbruyères, 1996) and shrimp species (Lavania-Baloo et al., 2014). Special attention should also be paid to the selection of appropriate macroalgal candidate for the IMTA system. Suitable seaweeds should be characterized by a high growth rate, productivity, nutrient uptake and insensitivity to high concentrations of ammonium (NH_4^+) (Grote, 2016; Elizondo-González et al., 2018). Among all seaweed species, green alga *Ulva* spp. and red algae *Gracilaria* spp. and *Porphyra* spp. are well-established aquaculture species. Their nutrient uptake ability and growth rates are high when compared to other seaweed species (Grote, 2016; Ashkenazi et al., 2019). Red alga *Palmaria palmata* is described as NH_4^+ -sensitive (Grote, 2016). Elizondo-González et al. (2018) showed that green macroalga *Ulva lactuca* removed nitrogen (80%) and phosphorus (64%) from shrimp's wastewater coming from the integrated recirculation system and improved their growth performance and the content of carotenoids. The same conclusion was reached by Lavania-Baloo et al. (2014): in the IMTA system, macroalgae *Gracilaria edulis* and *U. lactuca* removed significant ammonium amounts from shrimp wastewater (70% and 45%, respectively) and improved water quality, which is essential for shrimp growth and survival. Table 2 presents the examples of integrated multitrophic aquaculture in different areas of the world. China, Japan and South Korea dominate. Farms of fish, shellfish and seaweed are placed next to each other in bays and lagoons (Neori et al., 2004).

The IMTA system is more and more popular as evidenced by the number of published scientific papers concerning this topic. According to the Web of Science database (July 19, 2019), the number of papers concerning the bioremediation of aquaculture with seaweed was 70. The rationale, evolution and state of the art of the integrated aquaculture was described in detail by Neori et al. (2004). The IMTA system is the example of sustainable development of aquaculture (Chung et al., 2002; Fleurence et al., 2012; Marinho-Soriano et al., 2011). Seaweed cultivation combined with fed species in the integrated multi-trophic aquaculture is an important tool in environmental management. It improves ecological efficiency, sustainability and

Table 2 The examples of the integrated multitrophic aquaculture.

Seaweed	Aquaculture	Region	Reference
<i>Ulva lactuca</i> (G)	tiger shrimp	outdoor experimental setup, Malaysia	Lavania-Baloo et al. (2014)
<i>Gracilaria edulis</i> (R)			
<i>Ulva lactuca</i> (G)	shrimp	La Paz bay in Baja California Sur, Mexico	Elizondo-González et al. (2018)
<i>Ulva rigida</i> (G)	gilthead sea bream (<i>Sparus aurata</i>)	Haifa, Israel	Ashkenazi et al. (2019)
<i>Gracilaria conferta</i> (R)			
<i>Hypnea musciformis</i> (R)			
<i>Gracilaria lemaneiformis</i> (R)	fish (<i>Sebastodes fuscescens</i>)	Jiaozhou Bay, north China	Zhou et al. (2006)
<i>Gracilaria lichenoides</i> (R)	shrimp (<i>Litopenaeus vannamei</i>), fish (<i>Epinephelus awoara</i>)	Xiangshan Bay, Ningbo, China	Xu et al. (2008)
<i>Gracilaria caudata</i> (R)	microcrustacean (<i>Artemia franciscana</i>)	Brazil	Marinho-Soriano et al. (2011)
<i>Gracilaria verrucosa</i> (R)	fish – large yellow croaker (<i>Pseudosciaena crocea</i>)	Xiangshan harbor, China	Hou et al., 2012
<i>Gracilaria heteroclada</i> (R)			
<i>Eucheuma denticulatum</i> (R)	donkey's ear abalone (<i>Haliotis asinina</i>)	open sea Cebu, Philippines	Largo et al. (2016)
<i>Gracilaria lemaneiformis</i> (R)	fish (<i>Pseudosciaena crocea</i>)	Yantian Bay, China	Wei et al. (2017)
<i>Gracilaria lemaneiformis</i> (R)	fish (<i>Pseudosciaena crocea</i>), Japanese oyster (<i>Crassostrea gigas</i>), sea cucumber (<i>Apostichopus japonicas</i>)	Sansha Bay, an enclosed bay in China	Wu et al. (2015b)
<i>Laminaria japonica</i> (B)	shellfish (<i>Crassostrea gigas</i> , <i>Chlamys farreri</i>)	Sungo Bay, China	Zhang et al. (2009)

safeguards cost-efficient production ([Carmona et al., 2006; Grote, 2016](#); [Wei et al., 2017; Xu et al., 2008](#)). Marine aquaculture is a key future direction for the production of food ([Ashkenazi et al., 2019](#)).



4. Utilization of seaweeds from bioremediation

Seaweeds from the remediation of wastewater from industry, aquaculture, agriculture, and eutrophicated water could provide a significant source of biomass for the production of valuable products ([Bird et al., 2011, 2012](#); [Roberts, Paul, Bird, & de Nys, 2015c](#)). It is proposed that algae grown in wastewater can be used for the production of biofuels, biosorbents (e.g., biochar), and soil amendments etc., sometimes as feed additives for animals. Combining algal biomass production with wastewater treatment can reduce the cost of algae cultivation through minimization of freshwater consumption. This approach provides also a pathway to combatting industrial pollution and eutrophication ([Lyon, Ahmadzadeh, & Murry, 2015](#)). For example, [Roberts et al. \(2015c\)](#) cultivated macroalgae in contaminated ash water from a coal-fired power station. During macroalgal growth, the intracellular metal ions sequestration reduced their concentration in treated water. The authors proposed that enriched biomass be used for the production of biochar via slow pyrolysis and energy. Algal biochar has a low content of leachable metals and therefore can be used as an ameliorant for low-fertility soils. The bioremediation technology of wastewater combined with seaweeds cultivation (water recycling and biomass production) can be recommended for a water-limited industry (e.g., power stations). [Deniz and Ersanli \(2018\)](#) used the mixture of four species of marine seaweeds – green *Chaetomorpha* sp. and *Ulva* sp., red *Vertebrata* sp. and brown *Cystoseira* sp. to remove Cu(II) ions from aqueous medium. The maximum biosorption capacity was 180 mg of Cu(II) ions per gram of the biosorbent (for the optimal experimental conditions: pH 6, C_S : 0.1 g/L, C_0 : 10–30 mg/L, 2 h). The authors proposed to integrate this bioremediation system with biofuel production as sustainable waste management and renewable energy production. The loaded algal biomass can be incinerated to produce “bio-ore” and energy ([Brooks, Chambers, Nicks, & Robinson, 1998](#); [Roberts et al., 2015c](#)). The fully “metal-loaded” biosorbent may concentrate heavy metals a thousand fold from their concentration in aqueous solutions ([Davis et al., 2003](#)).

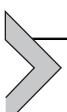
Special care should be taken when searching for new management methods of the algal biomass after bioremediation. Besides the removal of

biogens such as nitrogen and phosphorus, seaweeds can also bioaccumulate other elements that are present in water, for example toxic metal ions such as copper, cadmium, lead, zinc, etc. Therefore, before utilization, seaweed biomass should be examined for multielemental composition. Regular monitoring of minerals in seaweeds would prevent toxic and other undesirable situations (Makkar et al., 2016). The toxic metals content can disqualify algae from various applications, especially as components of human and animal food. For example, Amosu et al. (2016) showed that green *Ulva armoricana* could serve as a biological filter for dissolved nutrient from aquaculture effluents. Algal biomass had a relatively good quality with limited toxic metals content (Cu, Pb, Zn), but due to the presence of small amounts of cadmium, it cannot be used as a feed additive for livestock or the food industry. The authors recommend its application as a plant biostimulant.

Many of toxic elements that are removed by seaweeds from wastewater are typical heavy metals such as As, Cd, Hg, Pb, but some of them are microelements, e.g., Zn, Cu, Mn, Co that are necessary in small quantities for the proper growth and development of plants or animals (Bilal et al., 2018; Ozigit, Uyanik, Sahin, Yalcin, & Demir, 2017). Therefore, biomass enriched with elements via biosorption/bioaccumulation can be utilized for the production of components of fertilizers or feed additives with micro-elements (Bădescu, Bulgariu, & Bulgariu, 2017; Michalak et al., 2015b). Bădescu et al. (2017) used marine algal biomass (*Ulva* sp.) as biosorbent of Zn(II) ions. The enriched biomass was then applied as a fertilizer for the improvement of soil quality. In the biosorption experiment, *Ulva* sp. bound 29.6 mg of Zn(II) ions per gram of the biomass (for pH 5.5, C_0 : 10–220 mg/L, C_S : 8 g/L and the contact time 2 h). After 8 weeks from the use of Zn-loaded *Ulva*, the content of zinc in soil increased over four times. Tuhy, Samoraj, Michalak, and Chojnacka (2014) applied a similar approach. Baltic seaweeds and post-extraction residues obtained from the supercritical fluid extraction of seaweeds were used as biosorbents of Zn(II) ions in order to produce micronutrient fertilizer. Germination tests on garden cress (*Lepidium sativum*) showed that the application of enriched biomass caused the biofortification of plants in zinc. The weight of plants fertilized with seaweeds loaded with Zn(II) ions was higher than in the control group made up of conventional fertilizers such as inorganic salt and chelate.

Rarely are enriched algae used as feed additives for livestock although seaweeds have a long history of use in livestock feeding (ruminant, pig, poultry e.g., broilers, laying hens, horse, rabbit diet). Seaweeds contribute to the mineral, protein and energy requirements of livestock and due to

the content of the prebiotic compound, they enhance livestock production and health (Makkar et al., 2016). Michalak et al. (2011 and 2015a) used the mixture of green marine macroalgae *Ulva prolifera* and *Cladophora* sp., enriched with microelement ions Cu(II), Zn(II), Co(II), Mn(II), Cr(III) via biosorption as feed additives for laying hens and pigs. This biomass replaced inorganic salts traditionally used in animal feeding. It was shown that the bioavailability of microelements from algal feed additives was higher than in the case of inorganic form. Supplementation of enriched macroalgae resulted in higher microelement transfer to eggs of laying hens and meat of pigs. In the case of hens, seaweeds increased egg weight, eggshell thickness and body weight of hens and enhanced yolk color. These results show that seaweeds can be used both in aquaculture and in livestock feeding.



5. Bioremediation of contaminated soil

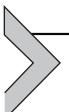
Soil bioremediation is a process in which living organisms have the ability to accumulate or degrade chemical contaminants into less toxic forms (Juwarkar, Singh, & Mudhoo, 2010). Seaweed ability to bioremediate contaminated soil can be limited by the pollutants content in the soil and the ability of algae to survive under these conditions. Green seaweeds (e.g., *Ulva* sp.) have been used for soil bioremediation mainly due to their wide distribution, fast growth, relatively simple structure and high tolerance to metal pollution (Abd-Elhady, 2015; Abd-Elhady & El-Zabalawy, 2014; Cheney et al., 2014; Farias et al., 2017). Farias et al. (2017) used macroalga *Ulva australis* for the removal of Zn(II) ions from the contaminated soil in the *in situ* assessment. *U. australis* thalli were transplanted to sites with different levels of metal pollution. It was shown that after 45 days, the content of zinc in the biomass was 700 mg/kg. During the first 12 days, zinc accumulation did not affect *U. australis* physiology (photosynthesis performance, photosynthetic pigment content, growth rate). After 45 days, Zn accumulation increased with the accompanying deterioration of the thalli, which led to the conclusion that a time period of 20 days was set for bioremediation. Abd-Elhady and El-Zabalawy (2014) and Abd-Elhady (2015) used dried seaweeds (*Ulva* sp. and *Gelidium* sp.) mixed with soil not only for the remediation of soil contaminated with Cu, Mn, Pb and Zn, but also to assess their effect on the growth (roots and shoots) and the content of the examined elements in the red radish (*Raphanus sativus* L.) and lettuce (*Lactuca sativa*). Pot

experiments showed that the addition of seaweeds to soil improved its total porosity, the content of available water and organic matter and increased the content of the examined elements in red radish and lettuce biomass. In the work of [Azmat and Askari \(2015\)](#), dried green seaweed (*Codium iyengri*) was added to soil to alleviate the lethal effect of Hg on the growth of fenugreek (*Trigonella foenumgraecum*). It was shown that seaweeds successfully controlled the mobility of mercury (binding of Hg by seaweeds) only at lower applied dose of metal (5, 10 and 15 mg/kg). At higher doses (20 and 25 mg/kg) seaweeds were effective to a much lesser extent: plants could not cope with the toxic effects of Hg.

[Kantachote et al. \(2004\)](#) used seaweeds to remove DDT from the environment, which is especially dangerous due to its low solubility, toxicity, bioaccumulation and biomagnification in the higher trophic levels. In the experiments, performed in a pilot-scale research bioremediation facility, it was shown that dried and ground seaweeds of green (*Ulva* sp.) and red algae (*Gelidium* sp.) enhanced the biodegradation of DDT in waterlogged soils. The highest percentages of DDT biodegradation (80%) after 6 weeks was found in the soil with the addition of 0.5% of seaweeds (among tested doses 1, 3, 5, 13 (*w/w*)). Anaerobic biodegradation of DDT occurred, probably due to an increased bacterial population after addition of seaweeds. [Cheney et al. \(2014\)](#) examined the uptake of PCBs contained in marine sediments by dead and live *Ulva rigida*. Macroalga was shown to be capable of removing PCBs in sediments at a rapid rate and under laboratory conditions the total PCBs uptake was significantly greater in live than dead biomass. [Cheney et al. \(2014\)](#) emphasized that the remediation of estuarine and coastal river sediments is much more difficult than that of soil due to the overlying water column and the possibility of contaminants resuspension during clean-up ([Gomes, Dias-Ferreira, & Ribeiro, 2013](#)).

Also seaweed biochar can be used for the bioremediation of anthropogenically impacted natural environments ([Bird et al., 2011](#)). In many countries, the disturbed land after mining has to be rehabilitated with native vegetation. This process can be difficult and slow due to absence or low content of nutrients and organic matter. Therefore it is proposed to apply algal biochar to enhance the rehabilitation of the stockpiled soil ([Roberts et al., 2015a](#)). [Roberts et al. \(2015a\)](#) used macroalgae (*Oedogonium*) cultivated additionally in wastewater at a coal-fired power station as a feedstock for the production of biochar, which reduced the germination time of the grass seeds and enhanced the growth and production of a native plant i.e. the Kangaroo grass (*Themeda australis*). Although laboratory experiments provide

useful information concerning the soil bioremediation with seaweeds, there is still a need to understand how macroalgae can perform this process under real field conditions.



6. Seaweeds in biomonitoring studies

As shown in previous sections, seaweeds have the ability to accumulate metal ions from the surrounding water (Ali, Idris, Ebrahim, & Eltayeb, 2017; Burger et al., 2007; García-Seoane, Fernández, Villares, & Aboal, 2018; Henriques et al., 2017; Singh & Prasad, 2015; van Ginneken & de Vries, 2018), which results from their excellent survival strategies that enable them to withstand the environmental stresses (Chan et al., 2006; Chaudhuri, Mitra, Havrilla, Waguespack, & Schwarz, 2007). These biological systems are able to detect any toxic, harmful or deleterious change in the environment and adapt to different environmental conditions (Ali et al., 2017). Additionally, seaweeds are sessile, constitute representatives of the study area and are abundant along most of the world's coasts (Chaudhuri et al., 2007). Therefore, algae are crucial in the biomonitoring of environmental pollution (biological monitoring) and have been used in biomonitoring studies since the 1950s (García-Seoane et al., 2018). Seaweeds constitute also the first level in the trophic chain: they are primary producers that are eaten by organisms on the higher trophic level, including people and livestock (Burger et al., 2007).

The analysis of aquatic components such as water or sediment by seaweeds can provide an overview of the contamination and quality of the environment (Chaudhuri et al., 2007; Ozyigit et al., 2017). García-Seoane et al. (2018) lists seaweed species that are most often used in biomonitoring studies. Some of the more important green seaweeds are *Ulva* sp., *Cladophora* spp., *Codium* spp., *Caulerpa* spp., *Chaetomorpha* spp., some of the most important brown seaweeds are *Fucus* spp., *Sargassum* spp., *Padina* spp., *Cystoseira* spp., *Ecklonia* spp., *Ascophyllum* spp., and some of the most important red seaweeds are *Gracilaria* spp., *Laurencia* spp., *Hypnea* spp., *Corallina* spp., *Porphyra* spp., *Gracilaria* spp., *Ceramium* spp. and *Phyllophora* spp. Green macroalgae e.g., *U. lactuca* are known to be good biomonitor of toxic metal ions, such as Cd, Hg, Pb (for example, Henriques et al., 2017; Ozyigit et al., 2017). Usually there is a close relation between the concentration of toxic metals in the surrounding water and in the living seaweed-biomass (van Ginneken & de Vries, 2018). García-Seoane et al. (2018) found that most

biomonitoring studies (97%) involved inorganic contaminants and very few organic contaminants (3%). Biomonitoring studies using macroalgae are conducted with the aim of detecting the presence of elements, mainly Cu, Zn, Cd, Pb, Fe, Mn, Ni, Cr, Co, N, As and Hg in the environment. In order to assure the sustainability and health of the aquatic environment, the concentrations of heavy metals should be regularly monitored (Chaudhuri et al., 2007; Ozyigit et al., 2017). Seaweeds will reflect any change in the marine environment (Chaudhuri et al., 2007). To perform the biomonitoring study correctly, the following factors should be considered: sampling site, number of sampling sites; temporal representativeness, timing of surveys and the selection of the seaweed species used as biomonitor (García-Seoane et al., 2018). García-Seoane et al. (2018) proposed the methodology for the biomonitoring with marine macroalgae. Biomonitoring based on seaweeds can be a promising and a reliable tool of quantifying the negative effect of the environmental contaminant (Ezeonu, Tagbo, Anike, Oje, & Onwurah, 2012).



7. Conclusions

Seaweeds have the capacity to remove heavy metal ions and nutrients from water and therefore can potentially be used in the bioremediation and biomonitoring of such pollutants. Marine macroalgae are an undiscovered or underestimated raw material that can clean industrial effluents, eutrophicated water, effluents from aquaculture including marine integrated multi-trophic aquaculture and polluted soils. Seaweeds can serve in environmental biotechnology as a dead (biosorption) or live (bioaccumulation) biomass. Waste streams especially from agriculture and aquaculture can constitute a nutrient source for macroalgae growth. This solution provides reuse options: algal biomass can be utilized for the production of fertilizers, feed additives, biofuels or additional value adding products. Waste can be treated with waste, which can solve many environmental problems. Wastewater treatment with seaweeds is an additional argument for the application of the marine resources in the generation of exploitable biomass.

Acknowledgments

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