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Sargassum-based potential biosorbent to tackle pollution in aqueous ecosystems – An overview

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ABSTRACT

The uncontrolled release of toxic pollutants related to anthropogenic processes has threatened biodiversity and the ecological integrity of aqueous ecosystems during years. The bioaccumulation and biomagnification of toxic pollutants at different trophic levels have raised concern. Several bioremediation approaches have been tested for efficient mitigation and removal of toxic compounds such as metal ions from aquatic environments. Biosorption by biodegradable and renewable sources such as micro and macroalgae biomass has an increasing scope. However, the biosorption mechanisms of *Sargassum* spp. have not been completely elucidated, and there are still some drawbacks to overcome. *Sargassum* spp. biomass has been recognized to be a natural, renewable, and cost-effective material to arrest pollutants from aqueous systems. This mini-review is a compendium that spotlights the potentialities of *Sargassum*-based biosorbents as an alternative for the removal of toxic contaminants from aquatic environments. Main biosorption mechanisms, key factors influencing biosorption, and the challenges regarding its implementation are highlighted with suitable examples.

1. Introduction

The accelerated industrial progress has resulted in massive pollution of all ecosystems, threatening environment integrity, biodiversity, and human health. Industrial development depends on the exploitation of compounds such as pesticides, polychlorinated biphenyls, heavy metals, halogenated aliphatics, phenols, polycyclic aromatics, among others. Due to their high toxicity, low degradation rate, and bioaccumulation through the trophic chains, these compounds trigger significant adverse effects on the environment and living organisms [1,2]. Pollutants usually end up in aqueous systems through leaching, atmospheric deposition, filtration, direct dumping, etc. (Fig. 1) [3].

There is an increasing interest in the recovery, removal and/or degradation of pollutants from the aquatic environment. Different physiochemical techniques, such as ion exchange, photocatalysis, membrane separation, filtration processing, coagulation/flocculation, and electrochemical methods, have been employed [1]. Nevertheless, physicochemical processes have presented limitations as chemical precipitation leading to the formation of toxic sludge, low efficiency in the total removal of contaminants, and high costs [3]. In this context, alternative methods are demanded a cheap and effective removal option and/or recovery of pollutants.

Algae biomass has been described to remove potentially toxic compounds from aqueous systems through biosorption, which is rapid, reversible, has minimal environmental impact, is a safe, economical, and efficient method [1,3]. Brown seaweed biomass, has gained recognition as a biosorbent (over other organisms biomass such as bacteria and fungi) for water bioremediation [4]. For brown seaweeds, the main mechanisms reported to remove pollutants in aqueous systems are based on (1) surface adsorption, which does not require living-biomass; and (2) bioaccumulation, which is metabolism dependent and requires living-biomass [5]. The surface adsorption has become the most used method to capture pollutants because of its cost–benefit relationship which is determined by the low-cost of non-living biomass maintenance and the high adsorption yields obtained by the algae biomass related to their complex cell wall properties (rich in alginate, fucoidan, and high

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Fig. 1. Various routes that may cause pollution to the aqueous ecosystem. Reprinted from Ref. [3] with permission from Elsevier. © 2019 Elsevier B.V.

content of carboxyl groups), that enhance its ability to uptake pollutants [3,4]. In this regard, *Sargassum* spp. biomass is a cheap, renewable, and natural material, which is becoming a pressing problem due to its unusual proliferation (bloom) in tropical seashores. Its abundant incidence elucidates a cost-effective alternative for the development of *Sargassum*-based biosorbents for the removal of toxic substances from aqueous environments [4]. Based on the literature, the utilization of *Sargassum* spp. as a biosorbent, has been successfully tested (Table 1). However, the mechanism in which the process takes place is still not fully understood, and some drawbacks need to be overcome to enhance *Sargassum* biomass biosorption efficiency [1,3]. This mini-review aims to spotlight the main mechanisms of surface biosorption of pollutants of *Sargassum* spp. biomass, the key factors that influence the biosorption process, potentialities *Sargassum* spp. have in different industries and the challenges of *Sargassum*-based biosorbents, that are becoming a promising alternative for the removal of toxic pollutants from aquatic environments.

2. Mechanisms of biosorption

Sargassum spp. are tolerant and resistant to heavy metals compared to green and red algae [6], and their biosorption properties are attributed to functionalities on their cell wall surface. Brown algae cell walls are more complex than fungi and bacteria. Their main components are cellulose, a structural homo-polysaccharide, fucoidan matrix as sulfated polysaccharides, and alginic acid, a biopolymer of mannuronic and guluronic acids. The composition of alginate from *Sargassum* spp. confers its high capacity for metal binding because it constitutes almost 40% of dry weight [7]. The functional groups create binding sites for metals making adsorption possible such as sulfonic acid from fucoidan, amino groups, carboxylic acid, and hydroxyl from alginic acid. High values of pH led to negative charges on these groups that allow reactions with protonated pollutants to trigger mechanisms of biosorption, with different physicochemical characteristics [8].

Biosorption mechanisms are categorized in an accurate system according to the adsorption processes on the algae surface. They are physisorption, microprecipitation, ionic exchange, and chemisorption (Fig. 2) [9]. Physisorption is non-specific in nature; results from electrostatic attraction and van der Waals interaction when the negative charges on the sorbent surface attract cationic contaminants. Micro-precipitation or surface precipitation is a process in which metal ion reacts with extracellular polymers to led crystallization. Ion exchange implied replacing metal ions with equivalent amounts of similarly charged ions into the adsorbent, that it could be a polymeric resin or the cell wall algae throughout an irreversible reaction. Chemisorption is highly specific in nature; involves a chemical reaction that includes covalent binding and complexation, where chelation results from metal ions binding to organic ligands into a similar ring structure [10,11]. Biosorption could be a combination of several mechanisms in an ordered manner following five steps: (1) cell surface penetration, (2) adsorption, (3) interaction with functional cell wall groups, (4) transfer metal to the cell surface, and (5) organic-metal bonding [12]. The immobilization of a polymeric matrix could improve the biosorbent functions in a continuous system such as a fixed column to treat effluents. *Sargassum* spp. cell walls can be readily solubilized and immobilized to remove light metals such as Na, K, Ca, and Mg due to calcium alginate composition as a target on the adsorption mechanism [7,13]. As an additional advantage, there is no need to regenerate *Sargassum* spp. biomass; since it is spreading and available at beaches [14].

3. Key factors that influence biosorption

The pH factor is considered the most critical in biosorption. High adsorption efficiency at a pH 7 has been reported using *Sargassum* spp. biomass with a maximum adsorption value of Cobalt (II) ions at 54.73 mg/g [15]. Nevertheless, lower pH values cause the repulsion between protonated carboxylic acids and heavy metal ions with positive charge leading to a low adsorption capacity; on the other hand, high pH values deprotonate hydroxyl, amines, and carboxyl functional groups promoting the formation of hydroxide anionic complexes which tend to precipitate impeding efficient adsorption [1,3].

In most of the cases, a high concentration of metal ions in effluents ends in an excellent performance of algae biomass adsorption. This effect occurs due to that the high ion concentration exceeds the mass transfer resistances between the biomass and the aqueous solution. Nonetheless, it does not follow a linear behavior, with a high initial metal ions concentration, the adsorption efficiency reaches the saturation of the biosorbent and stops the process [16]. Otherwise, a low concentration of metal ions assures higher concentrations removed, because the upper percentages of removal of ions could be considered as a low concentration effluent, the presence of metal ions must be below 20 mg/L [16].

Temperature significantly affects the thermodynamic behavior of biosorption as part of an endothermic process. However, high temperatures are not suggested as they could degrade algae biomass [17]. In some cases a positive effect of high-temperature values can trigger an improvement in the diffusion of the adsorbates over the superficial layer and inner pores of the biosorbent due to a decrease in the viscosity of the solution, it also increases the number of active sites available for adsorption, and enhance the stability of the connections through the metal ions and the functional groups of the biomass [12,16].

The contact period is a key factor in the efficacy of heavy metal ion adsorption. Biosorption is performed in two stages: a fast phase, where the ions adhere to the cell wall through the binding sites, and a slow phase that reaches the equilibrium by occupying all the active sites until saturation of the biosorbent [3]. In cases where biosorption is mediated by living algae, they can also bioaccumulate the ions and slowly will be used up by the algal cell [18]. For macroalgae species, the contact period

Table 1
Biosorption capacity of various *Sargassum*species to remove potentially toxic elements from aqueous ecosystems. ***IC**: ion concentration;**T**= temperature,**Ct**= contact time,**Bd**= biosorbent dosage.*

Potentially toxic Pollutant	Related toxic effects	*Sargassum*specie	Biosorption capacity (mg/g)	Factors	References
As (V)	Nervous system alterations, metabolic disorders, Cardiovascular and vascular diseases.	*Sargassum glaucescens*	207.30	pH = 5.9 IC = 120.3 ppm T = 25 °C Ct = 45 min Bd = 0.47 g/L	[1,30]
Hg (II)	Neurodegenerative diseases, digestive and immunological disorders	*Sargassum glaucescens*	147.05	pH = 5 IC = 200 ppb T = 25 °C Ct = 90 min	[1,31,32]
Cr (VI)	Carcinogenic, blood disorders, liver or kidney damage, neurological affection.	*Sargassum muticum*	196.10	pH = 2 IC = 20 ppm T = 20 °C Ct = 60 min Bd = 2 g/L	[1,33]
Co (II)	Neurological (visual and hearing impairment), cardiomyopathy, endocrine deficits.	*Sargassum* sp.	80.27	pH = 7 IC = 300 ppm T = 45 °C Ct = 1.5 h Bd = 1 g/L	[34,35]
Cd (II)	Adenocarcinoma, pulmonary and gastrointestinal swelling, kidney, bones and liver are also affected	*Sargassum filipendula*	103.50	pH = 6 IC = 100 ppm T = 35 °C Ct = 1 h Bd = 2 g/L	[1,36]
Cu (II)	Neurodegenerative diseases, carcinogenic, metabolic disorders, triggers atherosclerosis	*Sargassum fusiforme*	7.69	pH = 8-10 IC = 10 ppm T = 25 °C Ct = 1 h Bd = 2 g/L	[1,37]
Pb (II)	microvascular endothelium damage, alters immune system and nervous system, impairs mammalian spermatogenesis	*Sargassum filipendula*	367.94	pH = 5 IC = 100 ppm T = 35 °C Ct = 40min Bd = 2 g/L	[1,36]
Zn (II)	Liver and kidney failure, macular degeneration, prostate cancer, stomach and intestinal irritation, impotence, depression, ataxia	*Sargassum* sp.	1.39	pH = 3 IC = 10 mg/L T = 25 °C Ct = 1 h Bd = 1 g/L	[1,38]
Ni (II)	Allergic skin reaction, immunomodulatory and immunotoxic agent, carcinogenic, reproductive toxicants, stomach irritation, Kidney injury,	*Sargassum* sp.	71.66	pH = 5.0 IC = 100 ppm T = 30 °C Ct = 4 h Bd = 1 g/L	[37,39]
Mn (II)	Neural damage, hepatic and cardiovascular damage, testicular affection, impotence, decrease sperm mobility	*Sargassum hystrixalgae*	2.66	pH = 6.6 IC = 10 ppm T = 25 °C Ct = 120min Bd = 10 g/L	[40]

reported has not exceeded 4 h for biosorption [3,19]. This process will also depend on the relationship between the ion concentration and the contact area of the biosorbent leading to maximum contact time. The dose of the biosorbent has a tremendous impact on the biosorption process. Changes have been reported in the initial biosorbent dosage with an increase in the yield of Fe(II) ions biosorption usin *Sargassum hystrix* varying from 65 to 99% when the initial dose ranged from since 0.1–10 g/L [20]. Biosorption of Fe (III) ions using *Sargassum vulgare* have removed from 40 to 96% when a variation on the dosage was from 1 g/L to 5 g/L [21].

4. Miscellaneous potential of *Sargassum* spp.

The frequency and abundance of *Sargassum* spp. blooms in the Caribbean represent a threat to tourism and fisheries sectors which are the main economic activities of the region [22,23]. Different technologies have been implemented to add value to *Sargassum* biomass and mitigate its economic impact ensuring coastal sustainability [23].

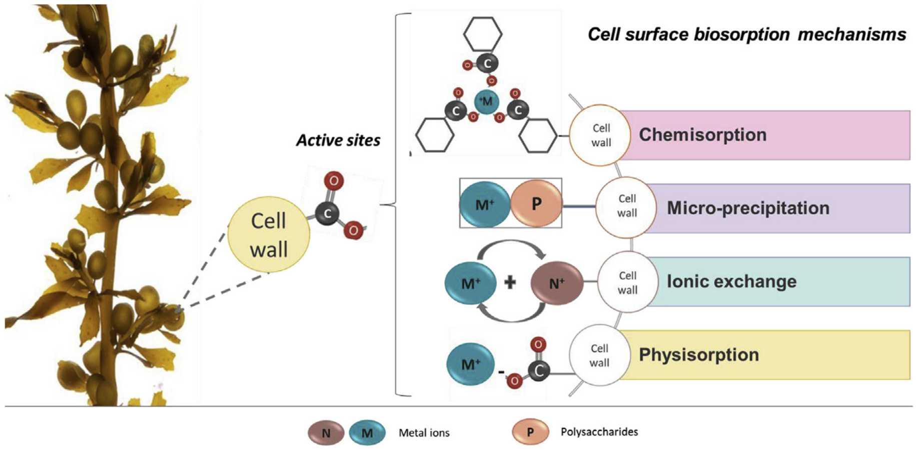

Fig. 2. Biosorption mechanisms related to the adsorption processes on the surface of *Sargassum* spp.

Sargassum has shown potential in different industrial application as growth plant stimulant, food supplement, energy source, heavy metal biosorbent, and other high-value compounds source [3,23,24].

Sargassum is considered a natural fertilizer in agriculture since the algae is rich in minerals, phenolic compounds and soluble polysaccharides, altogether helping to enhance productivity, enzymatic activity, and soil conditions [25]. *S. johnstonii* has been reported to increase essential mineral content (Mg, Na, Ca, K, and Zn) and the organic composition of the soil, improving water retention and soil structure. These conditions promotes the growth, flowering and fruiting of plants compared to unfertilized crops [23,26]. *Sargassum* biomass, as a biosorbent, also has affinity for macronutrients such as P and N, at the moment the biomass is immersed in fresh water, after removing salinity, the nutrients are released, and can be used as an inexpensive fertilizer [23,27].

As food supplement, *Sargassum* in its raw form is rich in dietary fiber, In Japan, around 10% of their dietary requirements are meet by *Sargassum* [23]. The Fatty acid profile of *Sargassum* spp. consist mainly in polyunsaturated fatty acids in an average ratio of 1.5:1 of omega-6 and omega-3, this amount justify its use as food supplement, since support cardio-vascular health [28]. Polysaccharide content of *Sargassum* spp. composed mostly by laminarin, alginate, fucoidan, and mannitol, makes this macro-algae a source of different products of food industry such as emulsifiers, encapsulants, and coating agents [23].

Energy is another field where *Sargassum* is being studied. The structural composition of this brown algae supports microbial degradation, which makes it a potential feedstock for bioenergy production through anaerobic digestion (AD). AD, results in biogas and an enriched (N and P) digestate. Biogas is a renewable energy source composed mainly by methane and carbon dioxide. Removing impurities, methane can be employed for heating, cooking and electricity production. The enriched digestate has potential as a fertilizer [23].

Sargassum biomass is also a source of several bioactive metabolites with wide application in cosmetic and pharmaceutical industries. Several biological activities are reported related to high-value metabolites of *Sargassum* spp [3]. Polyphenols are known to have antioxidant and antiviral activities and are used as UV-protectors. Pigments as fucoxanthin have hepatoprotective, anti-obesity and anticancer activities. Terpenoids are used as anti-inflammatory, skin protector and cardio protector. Polysaccharides can modulate immune response and are natural antimicrobial agents due its content of sulphate groups [3,23,29]. Above mentioned biological activities are just a few of the wide potential that *Sargassum* metabolites have in pharmaceutical industry. Overall, *Sargassum* biomass, is a cheap and renewable material that can be transform into different products with application in several industries, building an alternative to mitigate the economic impact this seaweed has in the Caribbean region.

5. Concluding remarks and future challenges

Currently, biosorption is known as an eco-friendly technology to remove trace metals from effluents, *Sargassum* spp. have been identified with high biosorption capacity due to its high content of polysaccharides such as alginate and fucoidans. Its bioremediation capacity depends on the functionalities on their cell wall surface and the interaction with pollutants. Ion concentration, pH, temperature, contact time, and biosorbent dosage are key factors that influence the biosorption mechanisms of *Sargassum* spp. biomass. Although *Sargassum*-based biosorbents exhibit a great potential to tackle pollutants in aqueous systems, some challenges need to be overcome to enhance its efficiency, among them: (1) storage and transportation of biomass, (2) the lack of multicomponent systems research, (3) the lack of scaled-up studies, and industrial effectiveness evaluation. Future trends point to enhance biosorption properties through the development of large-scale surface modification methods to enhance metal uptake. Biomass or polysaccharides immobilization and hybrid biosorption mechanisms using chemical and biological approaches are needed to improve the selectivity for specific pollutants with high biosorption capacity.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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