Heavy metals removal from contaminated solution using seaweed

Subjects: Engineering, Environmental
Contributor: Edward Hingha Foday Jr

Heavy metal contamination affects lives with concomitant environmental pollution, and seaweed has emerged as a remedy with the ability to save the ecosystem, due to its eco-friendliness, affordability, availability, and effective metal ion removal rate. Heavy metals are intrinsic toxicants that are known to induce damage to multiple organs, especially when subjected to excess exposure. With respect to these growing concerns, this review presents the preferred sorption material among the many natural sorption materials. The use of seaweeds to treat contaminated solutions has demonstrated outstanding results when compared to other materials. The sorption of metal ions using dead seaweed biomass offers a comparative advantage over other natural sorption materials. This article summarizes the impact of heavy metals on the environment, and why dead seaweed biomass is regarded as the leading remediation material among the available materials.

Keywords: heavy metals ; seaweed ; biosorption ; aqueous solution ; remediation

1. Structure and Classification of Seaweed

Seaweed does not have roots, but rather has holdfasts that anchor the seaweed to the bottom of the sea or ocean. These root-like holdfasts are composed of many finger-like components known as Haptera and are supported by a stalk or stem called a Stipe. The structure of the stem or stipe can be hard, filled with gas, soft or flexible, short, or long, and in some cases, they may be completely absent depending on the type of seaweed [1]. These stipes or stem-like structures are either filled with gas or empty. These are referred to as pneumatocysts, while the entire body of the seaweed is referred to as the thallus. Seaweed has leaves called blades, which assist in photosynthesis, although some seaweed species have only a single leaf, while others have many leaves. **Figure 1** below shows the physical structure of seaweed.

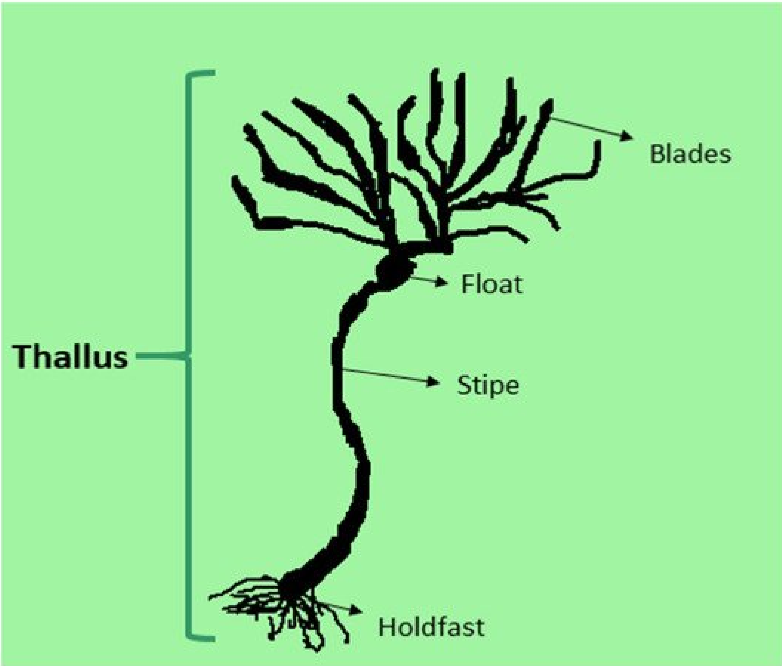

Figure 1. Structure of seaweed.

Seaweed is divided into three (3) main groups based on color characterization, namely: Brown (Phaeophyceae), Red (Rhodophyceae), and Green (Chlorophyceae) seaweeds [2]. Brown algae (Phaeophyta) have various physical appearances either in crust or filament form. Brown algae are multicellular and contain chlorophyll, which aids in photosynthesis, with fucoxanthin being the dominant pigment. Physically, brown algae can range from a large size (Kelp) of about 60 m long to as small as 60 cm [3]. Red algae (Rhodophyta) have chlorophyll in which phycocyanin and phycoerythrin are the dominant pigments responsible for red coloration. Red seaweeds are normally not actually red, but brownish-red or purple. Physically, red algae are smaller than brown algae in length [4]. Green seaweeds (chlorophyte) have chlorophyll, but with no dominant pigment justifying their green coloration; therefore, green seaweed is generally green. It is smaller in size than both red and brown seaweeds [5][6].

We further characterized seaweeds based on both their physical and chemical compositions as shown in **Table 1**. The alginate and the intercellular substance of the brown algae have high divalent cation uptakes. The cell walls of brown seaweeds are composed of cellulose, alginic acid, and polysaccharides, with alginates and sulfate being the dominant active groups [7]. The cell wall of red algae contains cellulose, but their biosorption capabilities can largely be attributed to sulfated polysaccharides made up of galactans. Similarly, the cell wall of the green algae contains cellulose with hydroxyl-proline glucosides; xylans and mannans are the main functional groups during biosorption [8][9].

Table 1. Characteristics of Seaweed.

Common Name (Phylum)	Body Form	Size	Pigments	Colour Composition	Cell Walls
Brown algae (Phaeophyta)	**Multicellular**	**60 cm–60 m**	**Chlorophyll, Fucoxanthin, and several other xanthophylls**	**Golden-brown, Greenish-brown**	**Cellulose, Alginate, Fucoidan**
Red algae (Rhodophyta)	**Multicellular**	**50 cm–2 m**	**Chlorophyll, Phycocyanin, Phycoerythrin, and several xanthophylls**	**Brownish red, Purple**	**Cellulose, Xylans, Galactans**
Green algae (Chlorophyta)	**Unicellular, Colonial, Filamentous, Multicellular**	**1–1000 µm**	**a and b Chlorophyll and several xanthophylls**	**Green**	**Cellulose Hydroxyl –proline glucosides β- xylans, β-mannans**

2. Seaweed: Metal Ion Biosorption Material

The treatment of contaminated solutions has been a burden to engineers and scientists over the years. Recently, seaweed has been proven to be more effective than other natural sorption materials. Some of the other natural sorption materials that have been used to elute metal ions are discussed in the next subsection. Remediation of aqueous solution from metal ions is of serious concern to environmentalists, considering the threat it poses to the purity of the natural environment [10]. The non-biodegradability, carcinogenicity, and toxicity of heavy metals make them harmful, and treatment of these heavy metals is essential [11]. Sorption has been proven to be a sustainable and effective method for treating heavy metals in aqueous solutions using natural biomass [12]. Based on these outstanding results, seaweed has emerged as the leading material, with a high rate of metal ion removal. The biosorption method is one of the simplest, cheapest, and most eco-friendly methods, and requires little or no nutrient addition. The effectiveness and efficiency of treatments for heavy metals are directly related to the type of sorbent used [13]. In short, the remediation of heavy metals using seaweed offers a more reliable, cheaper, and more effective means of heavy metal removal from aqueous solutions than the previous methods. Various mechanisms of seaweed biomass (electrostatic interaction, ion exchange, and complex formation) have been used in the biosorption process of heavy metals, and ion exchange has been widely used and is considered the most important among the list of mechanisms [14][15]. The cell walls of the algae possess polysaccharides and protein, which serve as binding sites for metal ion uptake [16]. There are several factors responsible for the sorption capability of a seaweed cell surface; among these factors are accessibility of binding groups for metal ions, the affinity constants of the metal with the functional group, the chemical state of these sites, the number of functional groups in the algae matrix, and the coordination number of the metal ion to be sorbed [17]. The metal biosorption ability of seaweed varies because of the heterogeneity of their respective cell wall composition. For example, brown, green, and red algae have high affinities for lead (Pb), copper (Cu), and cobalt (Co), respectively [7]. Physical or chemical treatment can enhance heavy metal uptake by seaweed, and the cell wall surface is modified, thereby providing additional binding sites for biosorption [7][18]. The physical treatment includes freezing, crushing, heating, and drying, as these increase the surface area on which biosorption can be achieved [18]. The most common seaweed pretreatments are glutaraldehyde, calcium-chloride ($CaCl_2$), formaldehyde, sodium hydroxide (NaOH), and hydrogen-chloride (HCl). Pretreatment with calcium-chloride (CaCl2) enhances calcium binding with alginate, which plays a pivotal role in ion exchange [19]. The crosslinking bond between hydroxyl and amino group is strengthened by formaldehyde and glutaraldehyde [20]. The electrostatic interactions of metal ion cations are increased by sodium hydroxide (NaOH), while at the same time providing optimal conditions for ion exchange, while hydrogen-chloride (HCl) dissolves the polysaccharides of the cell wall and also replaces light metal ions with a proton, thereby increasing the biosorption binding sites [7]. It is in this regard that we aim to showcase the comparative advantages of seaweed over other sorption materials in the removal of heavy metals.

3. Various Natural Materials Used for Sorption

In recent years, engineers and scientists have directed much effort towards identifying the most suitable biosorption materials. Among many materials, seaweed has been revealed to be the most suitable and effective natural material. **Table 2** shows some of the various other materials that have been used for the removal of metal ions.

Table 2. Various natural materials used for the removal of metal ions.

Materials Used	Heavy Metals	References
Polymers	**Fe and Cr**	[21]
Sawdust and tree barks	**Hg, Pb, and Zn**	[22]
Electronic waste along with galvanic wastes	**Cu, Ni, Mn, Pb, Sn**	[23]
charcoal:	**Cr(III)**	[24]
Clay	**Cr(III)**	[25]
Fungi	**Cr, Fe**	[26]
Dead biomass	**Cr**	[27]
Peat moss	**Cr, Fe**	[28]
Peanut shells, Rice husk, Straw, and walnut cover	**Cr, Cu, Ni**	[29]
Cocoa shell	**Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn**	[30]
Coconut husk	**Cr, As**	[29]
Caol and fly ashes	**Cr, Cu, Ni**	[31]
Banana pith and peels	**Ni, Pb**	[32]
Cassava fiber	**Pb, Co**	[33]
Chicken feathers	**Al, As**	[34]
Sheep manure wastes	**Ca, Cd**	[35]
Sunflower	**Co, Cr**	[36]
Rice byproducts	**Cu, Fe**	[37]
Orange peels	**Cu, Fe, Hg**	[38]
Palm kernel fiber	**Fe, Hg**	[29]
Grape stalks	**Cr, Fe, Hg**	[39]

As highlighted in **Table 2**, the use of different biomass (living or dead) for the removal of heavy metals has been studied over the years, and microalgae have stood out among the others. For non-living organisms, the cell surface involves different functional groups like amini, hydroxyl, sulfhydryl, phosphate, sulfate, and carboxyl groups [40]. Sawdust and tree barks are rich in tannin/lignin, and have been studied by Fiset and team [41], as they proved effective in metal adsorption. The tannin is an active species during the metal adsorption (ion exchange) process because of the polyhydroxy polyphenol groups [42]. Lignin, which is extracted from black liquor and is also a waste product of the paper industry, has been considered for the removal of metals (Hg, Pb, and Zn) [43]. Alcohols, acids, aldehydes, ketones, phenol, hydroxides, and ethers are all polar functional groups of lignin that have varying metal-binding capabilities [44]. Phytoremediation or phytofiltration of metal-contaminated effluents have been tested and proven successful. Some examples of aquatic plants with such ability are *Ceratophyllum demersum*, *Lemna minor, and Myriophyllum spicatum* [45]. Cellular components such as amide, imine, imidazol moieties, carboxyl, hydroxyl, sulfate, sulfhydryl, phosphate of these plants have high metal-binding properties, as reported by Gardea and team [46]. Chitin and chitosan have also been used to treat metal ions in wastewater. Chitin, which is the second-most abundant natural biopolymer after cellulose, is commonly found in the exoskeletons of crustaceans and shellfish, while Chitosan is produced by alkaline N-deacetylation of chitin [47]. Similarly, peat moss has been studied based on heavy metal decontamination of wastewater. It is a complex material with both lignin and cellulose as its main constituents, which contain polar functional groups [48]. Plenty of other agricultural waste, such as rice residues, fruit and vegetable peels, tea/coffee residues, and coconut husks, have also been used for metal ion retention. Most of the materials have polyhydroxy, polyphenol, carboxylic, and amino groups, which play key roles in the metal adsorption process [30]. Animal bones, clay, human hair, and teeth have all been used to treat metal ions, but have not been effective or efficient when compared with seaweed [49]. In conclusion, the above-discussed natural sorption materials have not been effective either in terms of metal ions removal rate or socio-economic benefit when compared to seaweed.

References

1. Mahadevan, K. Seaweeds: A sustainable food source. In Seaweed Sustainability; Elsevier BV: Manchester, UK, 2015; pp. 347–364.
2. Collins, K.G. An investigation of the prebiotic potential and gut health benefits of Irish seaweeds. Univ. Coll. Cork 2017, 371, 31–35.
3. Gade, R.; Tulasi, M.S.; Bhai, V.A. Seaweeds: A novel biomaterial. Int. J. Pharm. Pharm. Sci. 2013, 5, 975–1491.
4. Harbo, J.R.; Harris, J.W. Heritability in Honey Bees (Hymenoptera: Apidae) of Characteristics Associated with Resistance to Varroa jacobsoni(Mesostigmata: Varroidae). J. Econ. Entomol. 1999, 92, 261–265.
5. Davis, T.A.; Volesky, B.; Mucci, A. A review of the biochemistry of heavy metal biosorption by brown algae. Water Res. 2003, 37, 4311–4330.
6. Bittner, L.; Payri, C.; Couloux, A.; Cruaud, C.; De Reviers, B.; Rousseau, F. Molecular phylogeny of the Dictyotales and their position within the Phaeophyceae, based on nuclear, plastid and mitochondrial DNA sequence data. Mol. Phylogenetics Evol. 2008, 49, 211–226.
7. Romera, D.E.; González, F.; Ballester, A.; Blázquez, M.L.; Muñoz, J.A. Biosorption with Algae: A Statistical Review. Crit. Rev. Biotechnol. 2006, 26, 223–235.
8. Yalçın, S.; Sezer, S.; Apak, R. Characterization and lead (II), cadmium (II), nickel (II) biosorption of dried marine brown macro algae Cystoseira barbata. Environ. Sci. Pollut. Res. 2012, 19, 3118–3125.
9. Sheng, P.X.; Ting, Y.-P.; Chen, J.P.; Hong, L. Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: Characterization of biosorptive capacity and investigation of mechanisms. J. Colloid Interface Sci. 2004, 275, 131–141.
10. Adamu, C.; Nganje, T.; Edet, A. Heavy metal contamination and health risk assessment associated with abandoned barite mines in Cross River State, southeastern Nigeria. Environ. Nanotechnol. Monit. Manag. 2015, 3, 10–21.
11. Badruddoza, A.Z.M.; Shawon, Z.B.Z.; Tay, W.J.D.; Hidajat, K.; Uddin, M.S. Fe3O4/cyclodextrin polymer nanocomposites for selective heavy metals removal from industrial wastewater. Carbohydr. Polymers 2013, 91, 322–332.
12. Turan, N.G.; Mesci, B. Use of Pistachio Shells as an Adsorbent for the Removal of Zinc(II) Ion. CLEAN—Soil Air Water 2011, 39, 475–481.
13. Pozdniakova, T.A.; Mazur, L.P.; Boaventura, R.A.; Vilar, V.J. Brown macro-algae as natural cation exchangers for the treatment of zinc containing wastewaters generated in the galvanizing process. J. Clean. Prod. 2016, 119, 38–49.
14. Mata, Y.; Blázquez, M.; Ballester, A.; González, F.; Muñoz, J.A. Characterization of the biosorption of cadmium, lead and copper with the brown alga Fucus vesiculosus. J. Hazard. Mater. 2008, 158, 316–323.
15. Michalak, I.; Chojnacka, K. Interactions of metal cations with anionic groups on the cell wall of the macroalga Vaucheria sp. Eng. Life Sci. 2010, 10, 209–217.
16. Gupta, V.; Rastogi, A. Biosorption of lead from aqueous solutions by green algae Spirogyra species: Kinetics and equilibrium studies. J. Hazard. Mater. 2008, 152, 407–414.
17. Mehta, S.K.; Gaur, J.P. Use of Algae for Removing Heavy Metal Ions From Wastewater: Progress and Prospects. Crit. Rev. Biotechnol. 2005, 25, 113–152.
18. Errasquín, E.L.; Vázquez, C. Tolerance and uptake of heavy metals by Trichoderma atroviride isolated from sludge. Chemosphere 2003, 50, 137–143.
19. Bishnoi, N.R.; Kumar, R.; Kumar, S.; Rani, S. Biosorption of Cr(III) from aqueous solution using algal biomass spirogyra spp. J. Hazard. Mater. 2007, 145, 142–147.

20. Ebrahimi, B.; Shojaosadati, S.; Ranaie, S.; Mousavi, S. Optimization and evaluation of acetylcholine esterase immobilization on ceramic packing using response surface methodology. Process. Biochem. 2010, 45, 81–87.
21. Pathe, P.P.; Nandy, T.; Kaul, S.N.; Szpyrokwicz, L. Chromium recovery from chrome tan wastewater. Int. J. Environ. Stud. 1996, 51, 125–145.
22. Lichtfouse, E.; Elbisser, B. 2nd European Meeting on Environmental Chemistry. In Proceedings of the 2nd European Meeting on Environmental Chemistry, Dijon, France, 12–15 December 2001; p. 273.
23. Vegliò, F.; Quaresima, R.; Fornari, P.; Ubaldini, S. Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning. Waste Manag. 2003, 23, 245–252.
24. Dahbi, S.; Azzi, M.; Saib, N.; De la Guardia, M.; Faure, R.; Durand, R. Removal of trivalent chromium from tannery waste waters using bone charcoal. Anal. Bioanal. Chem. 2002, 374, 540–546.
25. Park, S.-J.; Jung, W.-Y. Removal of chromium by activated carbon fibers plated with copper metal. Carbon Lett. 2001, 2, 15–21.
26. Bai, R.; Abraham, T. Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of Rhizopus nigricans. Water Res. 2002, 36, 1224–1236.
27. Chong, K.H.; Volesky, B. Metal biosorption equilibria in a ternary system. Biotechnol. Bioeng. 1996, 49, 629–638.
28. Lee, S.-J.; Park, J.H.; Ahn, Y.; Chung, J.W. Comparison of Heavy Metal Adsorption by Peat Moss and Peat Moss-Derived Biochar Produced Under Different Carbonization Conditions. Water Air Soil Pollut. 2015, 226, 9.
29. Ofomaja, A.; Ho, Y.-S. Effect of pH on cadmium biosorption by coconut copra meal. J. Hazard. Mater. 2007, 139, 356–362.
30. Meunier, N.; Laroulandie, J.; Blais, J.; Tyagi, R. Cocoa shells for heavy metal removal from acidic solutions. Bioresour. Technol. 2003, 90, 255–263.
31. Tan, L.C.; Choa, V.; Tay, J.H. The Influence of pH on Mobility of Heavy Metals from Municipal Solid Waste Incinerator Fly Ash. Environ. Monit. Assess. 1997, 44, 275–284.
32. Foday Jr, E.H.; Ramli, N.A.S.; Ismail, H.N.; Malik, N.A.; Basri, H.F.; Aziz, F.S.A.; Nor, N.S.M.; Jumhat, F. Municipal solid waste characteristics in Taman Universiti, Skudai, Johore, Malaysia. J. Adv. Res. Des. 2017, 38, 13–20.
33. Abia, A.; Asuquo, E. Lead (II) and nickel (II) adsorption kinetics from aqueous metal solutions using chemically modified and unmodified agricultural adsorbents. Afr. J. Biotechnol. 2006, 5, 1475–1482.
34. Al-Asheh, S.; Banat, F.; Al-Rousan, D. Adsorption of Copper, Zinc and Nickel Ions from Single and Binary Metal Ion Mixtures on to Chicken Feathers. Adsorpt. Sci. Technol. 2002, 20, 849–864.
35. Abu Al-Rub, F.A.; Kandah, M.; Al-Dabaybeh, N. Competitive Adsorption of Nickel and Cadmium on Sheep Manure Wastes: Experimental and Prediction Studies. Sep. Sci. Technol. 2003, 38, 483–497.
36. Özdemir, N.; Horn, R.; Friedt, W. Construction and characterization of a BAC library for sunflower (Helianthus annuus L.). Euphytica 2004, 138, 177–183.
37. Ajmal, M.; Rao, R.A.K.; Anwar, S.; Ahmad, J.; Ahmad, R. Adsorption studies on rice husk: Removal and recovery of Cd(II) from wastewater. Bioresour. Technol. 2003, 86, 147–149.
38. Ajmal, M.; Rao, R.A.K.; Ahmad, R.; Ahmad, J. Adsorption studies on Citrus reticulata (fruit peel of orange): Removal and recovery of Ni(II) from electroplating wastewater. J. Hazard. Mater. 2000, 79, 117–131.
39. Fiol, N.; Villaescusa, I.; Martínez, M.; Miralles, N.; Poch, J.; Serarols, J. Sorption of Pb (II), Ni (II), Cu (II) and Cd (II) from aqueous solution by olive stone waste. Sep. Purif. Technol. 2006, 50, 132–140.
40. Kapoor, A.; Viraraghavan, T. Heavy metal biosorption sites in Aspergillus niger. Bioresour. Technol. 1997, 61, 221–227.
41. Vaishya, R.; Prasad, S. Adsorption of copper (II) on sawdust. Indian J. Environ. Prot. 1991, 11, 284–289.
42. Vázquez, G.; Antorrena, G.; González-Álvarez, J.; Doval, M. Adsorption of heavy metal ions by chemically modified Pinus pinaster bark. Bioresour. Technol. 1994, 48, 251–255.
43. Srivastava, S.K.; Gupta, V.K.; Mohan, D. Removal of Lead and Chromium by Activated Slag—A Blast-Furnace Waste. J. Environ. Eng. 1997, 123, 461–468.
44. Bailey, S.E.; Olin, T.J.; Bricka, R.; Adrian, D. A review of potentially low-cost sorbents for heavy metals. Water Res. 1999, 33, 2469–2479.
45. Keskinkan, O.; Goksu, M.; Basibuyuk, M.; Forster, C. Heavy metal adsorption properties of a submerged aquatic plant (Ceratophyllum demersum). Bioresour. Technol. 2004, 92, 197–200.

46. Gardea-Torresdey, J.; Peralta-Videa, J.; Montes, M.; de la Rosa, G.; Corral-Diaz, B. Bioaccumulation of cadmium, chromium and copper by Convolvulus arvensis L.: Impact on plant growth and uptake of nutritional elements. Bioresour. Technol. 2004, 92, 229–235.
47. Dumitriu, S. Polysaccharides as Biomaterials. In Polymeric Biomaterials, Revised and Expanded; CRC Press: New York, NY, USA, 2001; pp. 15–76.
48. Brown, P.; Gill, S.; Allen, S.J. Determination of optimal peat type to potentially capture copper and cadmium from solution. Water Environ. Res. 2001, 73, 351–362.
49. Celis, R.; Hermosín, M.C.; Cornejo, J. Heavy Metal Adsorption by Functionalized Clays. Environ. Sci. Technol. 2000, 34, 4593–4599.