



Marine algae as bio-sorbents

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Abstract

Algae have received increasing attention for heavy metal removal and recovery due to their good performance, low cost and large available quantities. The algal biosorbent contains variety of functional sites including carboxyl, imidazole, sulphhydryl, amino, phosphate, sulfate, thioether, phenol, carbonyl, amide and hydroxyl moieties. Algal biosorption is dependent on various parameters such as pH, biomass concentration, temperature, contact time and initial concentration of metal ion in the solution. Brown algae stand out as very good biosorbents for heavy metals compared with red and green algae. In this paper, based on the literatures and research results, the marine algae used in biosorption for heavy metal removal were presented. This paper represents marine algae as the potential bioadsorbents for the removal of heavy metal ions from aqueous solutions.

Introduction

Biosorption can be defined as the removal of metal or metalloid species, compounds and particulates from solution by biological material (Jianlong and Can , 2009) Heavy metal pollution is one of the most important environmental problems today. With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc., heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries (Wang and Chen, 2006). Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. Faced with more and more stringent regulations, nowadays heavy metals are the environmental priority pollutants and are becoming one of the most serious environmental problems. So these toxic heavy metals should be removed from the wastewater to protect the people and the environment.

In recent years, applying biotechnology in controlling and removing metal pollution has been paid much attention, and gradually becomes hot topic in the field of metal pollution control because of its potential application. Alternative process is biosorption, which utilizes various certain natural materials of biological origin, including bacteria, fungi, yeast, algae, etc. These biosorbents possess metal-sequestering property and can be used to decrease the concentration of heavy metal ions in solution from ppm to ppb level. (Jianlong and Can , 2009).

Algae are of special interest in search for and the development of new biosorbents materials due to their high sorption capacity and their ready availability in practically unlimited quantities in the seas and oceans (Rincon *et al.*, 2005). However, there are few publications on biosorption with algae as compared to those using other biomass (mainly fungi and bacteria), and there is still fewer for multi metallic systems (Romera *et al.*, 2006). The topic is relatively novel, with exponential growth of interest throughout the scientific community in the last few years. According to the statistic review on biosorption, algae have been less used as biosorbent material than other kinds of biomass (Romera *et al.*, 2006). Algal biosorption is dependent on various parameters such as pH, biomass concentration, temperature, contact time and initial concentration of metal ion in the solution. The potential metal binding groups present on the cell surface of the algal species include carboxyl, imidazole, sulphhydryl, amino, phosphate, sulfate, thioether, phenol, carbonyl, amide and hydroxyl moieties.

Performance of Algae

According to Brinza *et al.*, 2007, higher metal uptake capacity has been found for brown algae than for red and green algae . Because they offer better sorption than red or green algae (Romera *et al.*, 2006). Volesky and his colleagues have

performed many researches on brown algae biosorption characteristics, especially Sargassum sp.(Davis *et al.*, 2004; Diniz and Volesky, 2005; Volesky *et al.*, 2003). Kishore *et al.*, 2013 performed the entrapment of marine microalga, *Isochrysis galbana*, for biosorption of Cr(III) from aqueous solution it's isotherms and spectroscopic characterization studies. Sarada *et al.*, 2014, studied Cadmium removal by macroalgae *Caulepra fastigiata*, it's characterization, Kinetic, isotherm and Thermodynamic studies. Davis *et al.*, 2003, has published a review of the biochemistry of heavy metal biosorption by brown algae. Brinza *et al.*, (2007) reviewed some marine micro and macro algal species as biosorbents for heavy metal ions. (Table-1). These algae were reported to be able to adsorb one or more heavy metal ions, including K, Mg, Ca, Fe, Sr, Co, Cu, Mn, Ni, V, Zn, As, Cd, Mo, Pb, Se, Al, with good metal uptake capacity (Brinza *et al.*, 2007).

Table.1.The maximum biosorption capacity (qmax) of some marine algae (unit: mmol g⁻¹)

	Pb	Cd	Ni	Cu	Zn
Micro Algae					
<i>Chlamydomonas reinhardtii</i>	0.23	0.2	0.17		0.16
<i>Chlorella salina</i>	0.24	0.44		0.55	0.12
<i>Chlorella sorokiniana</i>		0.34	0.12	0.18	
<i>Chlorella vulgaris</i>	0.46	0.29	0.31	0.25	0.18
<i>Chlorella miniata</i>			0.237	0.366	
<i>Chlorococcum sp.</i>	0.23	0.15	0.27	0.36	0.21
<i>Cyclotella cryptica</i>	0.42		0.14	0.33	0.1
<i>Gloeoecystis planctonica</i>	0.21	0.06	0.11		0.18
<i>Lynghya taylorii</i>	0.84	0.32	0.43		0.37
<i>Microcystis aeruginosa</i>	0.35		0.21	0.37	0.23
<i>Phaeodactylum tricornutum</i>	0.36	0.23	0.19		0.37
<i>Porphyridium purpureum</i>	0.33		0.2		0.25
<i>Scenedesmus obliquus</i>			0.51		
<i>Scenedesmus quadricauda</i>	0.45	0.11			0.35
<i>Scenedesmus subspicatus</i>	0.25			0.22	
<i>Spirogyra sp.</i>	0.49	0.27	0.12		0.23
<i>Spirulina platensis</i>	0.38	0.29	0.4		0.27
<i>Stichococcus bacillaris</i>	0.19	0.24	0.09		0.07
<i>Stigeoclonium tenue</i>	1.34	0.24		0.13	
Macroalgae					
<i>Ascophyllum nodosum</i>	1.31	0.33	1.34		
<i>Chaetomorpha linum</i>		0.48		0.27	
<i>Cladophora crispata</i>		1.27			0.45
<i>Cladophora fascicularis,</i>			0.23		0.35
<i>Codium fragile</i>		0.08			
<i>Colpomenia sinuosa,</i>	0.03			0.34	
<i>Corallina officinalis</i>		0.26			0.22
<i>Ecklonia sp.</i>	0.23			0.11	
<i>Fucus vesiculosus</i>	0.39		1.10	0.15	

<i>Fucus ceranoides</i>	0.25		0.17		0.16
<i>Fucus serratus</i>	0.27	0.17			0.11
<i>Galaxaura marginata</i>	0.121		0.18		
<i>Gracilaria corticata</i>	0.20			0.16	
<i>Padina gymnospora</i>	0.31		0.17		0.25
<i>P.tetrastomatica</i>	1.04	0.53			
<i>Porphyra columbina</i>		0.40			
<i>Sargassum sp.</i>	1.59	0.74	0.40	1.30	0.22
<i>Sargassum fluitans</i>	1.59		0.40		
<i>Sargassum natans</i>	1.14	1.13	0.40		
<i>S.vulgare</i>	1.10		0.08		
<i>Ulva lactuca</i>	0.61	0.45			0.34
<i>Undaria pinnatifida</i>	1.94	0.36			

Chojnacka *et al.* (2005) reported the biosorption performance of Cr³⁺, Cd²⁺ and Cu²⁺ ions by blue-green algae *Spirulina* sp. Based on the statistical analysis using biosorption data of 37 different algae (20 brown algae, 9 red algae and 8 green algae) from 214 references collected, a statistical review of biosorption of algae in the form of dead biomass were given by Romera *et al.*, (2006). The available data of maximum sorption capacity (q_{max}) for Cd²⁺, Cu²⁺, Ni²⁺, Pb²⁺ and Zn²⁺ were listed in the review. Brown algae stand out as very good biosorbents for heavy metals. Algae present a high affinity for Pb, followed by cadmium, copper, nickel and zinc, all of which present very similar values. The best performer for metal biosorption by brown algae is lead (Romera *et al.*, 2006). Romera *et al.* (2006) summarized the results achieved with brown algae, green algae, and red algae. It was found that the average sorption capacity of red algae was lower (Table-2).

Table .2.The average sorption capacity of Algae

	Cd	Ni	Zn	Cu	Pb
Red Algae	0.20	0.27			0.65
Green Algae	0.6	0.51	0.37	0.50	0.81
Brown Algae	0.92	0.84	0.67	1.01	1.23

The differences may be due to both the experimental conditions of each work and the chemical composition of the corresponding cell walls. Baran *et al.* (2005) reported that the maximum sorption capacity of *Halimeda tuna*, *Sargassum vulgare*, *Pterocladia capillacea*, *Hypnea musciformis*, *Laurencia papillosa* for Cr⁶⁺ were 2.3, 33.0, 6.6, 4.7 and 5.3 mg g⁻¹, respectively. The results showed that *S. vulgare* was suitable for removing chromium from aqueous solution. Taking Cu(II) as an example, the uptake capacity (expressed as q_{max} values) by various algal species were (q_{max}: mmol Cu/g): *A. nodosum* (Brown algae: 0.99), *Caulerpa lentillifera* (Green macroalgae: 0.13), *C. vulgaris* (Green microalgae: 0.67, 1.40), *Durvillaea potatorum* (Brown algae: 1.30), *Ecklonia radiata* (Brown algae: 1.11), *Glacilaria* sp. (Red macroalgae: 0.59), *Padina* sp. (Brown algae: 0.80, 1.14), *Sargassum filipendula* (Brown algae: 0.98), *Sargassum fluitans* (Brown macroalgae: 0.80, 0.96), *Sargassum* sp. (Brown algae: 0.99, 1.48), *S. vulgare* (Brown algae: 0.93). *Spirulina* sp., (Blue green algae: 0.004), *Ulothrix zonata* (Green macroalgae: 2.77), *Ulva* sp. (Green macroalgae: 0.75) (Brinza *et al.*, 2007). Murphy *et al.* (2007) also studied several dried biomass of the marine macroalgae, *Fucus spiralis* and *Fucus vesiculosus* (brown), *Ulva* spp. (Green), *Polysiphonia palmata* and *Polysiphonia lanosa* (red), in terms of their Cu(II) biosorption performance. *Ulva* spp. performed extremely efficiently in sequestering copper ions (0.326 mmol g⁻¹), may be due to its high uronic acid content.

The sources and type of biosorbent play a major role in determining the overall cost of the biosorbent material. If the biomass needs to be specifically cultured for this purpose, manufacturers will incorporate maintenance and production expenses in the total cost, as well as a commercial fee. These costs can be minimal where certain biomass types such as photo-autotrophic algae (e.g., *Chlorella* and *Oscillatoria* spp.) can be successfully grown for large-scale commercial use due to their minimal

growth requirements (water, sunlight and CO₂). Marine algae such as *S. fluitans* and *A. nodosum* have shown biosorptive potential although the costs of harvesting the biomass may prove inhibitory to its application.

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