



Metal sorption by algal biomass: From batch to continuous system



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ABSTRACT

Algal biomass possesses tremendous metal binding ability and therefore has great potential for cleaning these pollutants from wastewaters. The algal cell wall and exopolymers contain diverse functional groups which confer negative charge to cell surface. Since metal ions in water are generally in cationic form, they are adsorbed onto the cell surface. Biosorption of metal ions from aqueous solution is influenced by various factors, such as, pH, charge density of metal ion, concentration of metal ion, concentration of interfering metal ions, nutrient availability, nature of biomass, culture age, temperature and contact time. Batch studies are very important for collecting information for subsequent application on a large scale. Continuous flow studies, like those conducted in packed bed column, seem more efficient and economically feasible than the batch operation for metal sorption. Various kinds of sorption isotherms have been used for the assessment of maximum sorption capacity. The data of metal sorption obtained from continuous system are generally expressed in the form of breakthrough curves. The shape and size of breakthrough curve is influenced by several factors, such as, metal concentration, flow rate, bed height, size of biosorbent particle, solution composition, and packing of column/density biosorbent in the column. Adam-Bohart, Thomas, mass transfer model, advection–dispersion–reaction equation and bed-depth–service-time model have been developed for elucidating breakthrough curve. However, new approaches, such as artificial neural networking and response surface methodology need adequate attention for modeling of breakthrough curves and metal sorption in multi-metal systems.

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1. Introduction

Heavy metal pollution is an important environmental problem due to toxic and non-biodegradable nature of these pollutants, and also because of buildup of their concentration along the producer–consumer network [25,87,130]. Conventional methods for metal removal from industrial wastewaters are based on physico-chemical processes, such as, oxidation and reduction, chemical precipitation, filtration, electro-chemical treatment, evaporation and reverse osmosis, and are not cost-effective [1,41]. These methods are also not efficient when metal concentration in the solution ranges from 1 to 100 mg l⁻¹ [1]. Owing to inherent problems with conventional methods, considerable emphasis is nowadays being placed on exploitation of metal binding ability of biomass for the treatment of metal enriched wastewaters [36,42,68,89,99,134].

The phenomenon of metal binding by dead biomass is well known as biosorption. It includes passive mechanisms of metal binding that are not driven by metabolism [1,25,128]. Biosorption is entirely a solid–liquid phase interaction of biomass and metal ions, and thus very well matches with the binding of metal ions by ion-exchange resins. Metal binding by resins mainly involves ion-exchange, whereas biosorption is a consequence of simultaneous operation of several processes, such as, physical adsorption, ion-exchange, chelation, complexation, and micro-precipitation. [42]. Sometimes, the term biosorption has also been used for describing metal removal by live biomass, which includes both adsorption and uptake of metal ions. It should, however, be kept in mind that uptake is energy-mediated transport of metal ions across the cell membrane [33,89,124,134].

Metal sorption abilities of different organisms have been recently reviewed by several workers [1,30,39,56,89,90,104,134]. All these reviews conclude that dead biomass of microorganisms, belonging to diverse taxonomic groups, such as, bacteria, cyanobacteria, fungi, and algae, have enormous ability to bind metal ions even from very low concentrations in the external solution. Volesky [128] has clearly pointed out that biosorption is important for removing toxic metal ions from wastewater as also for concentration and recovery of precious metals, such as, gold, silver and radionuclides. Won et al. [138] have also highlighted various specifications of biosorbents for the recovery of precious metals.

Large-scale use of biosorption process will definitely need a large amount of biomass. The biomass of algae, including cyanobacteria (formerly known as blue-green algae), can be easily obtained from nature, or quickly raised in mass culture due to their short doubling time. The biomass producing systems are essentially solar-driven system, which can be open tank or pond, and depend on input of some essential mineral nutrients for proper growth [23,24].

Algal biomass contains a great apportionment of cell wall material, which possesses excellent metal binding properties. Some algae possess greater metal binding abilities than commercial ion-exchange resins. For instance, *Sargassum natans* and *Ascophyllum nodosum* outperformed ion exchange resins in sequestering Au(II) and Co(II), respectively, from solution [78]. These seaweeds have alginate and extracellular

polysaccharides as the major components of their cell wall, which play a predominant role in metal sequestration [31]. Bertagnolli et al. [14] have shown excellent removal of Cr(III) by alginate extracted from *Sargassum filipendula*. Recently, Oliveira et al. [97] have characterized La(III) sorption by *Sargassum* sp. using SEM/EDX. Marine green algae also show tremendous ability to accumulate various metal ions [37,62,63,125]. Freshwater green microalgae, such as, species of *Chlorella*, *Scenedesmus* and *Chlamydomonas*, also possess excellent metal sorption ability as evidenced by their high q_{max} (the parameter reflecting maximum metal sorption capacity). Birungi and Chirwa [15] have reported biosorption of La(III) by freshwater algal materials. Zhou et al. [141] reported almost complete removal of Zn and Cu by *Chlorella pyrenoidosa* and *Scenedesmus obliquus*. Likewise, *Chlorella miniata* significantly removed Cr(III) [50]. Microalgae adsorb great amounts of metal ions because they possess large surface area. Some freshwater filamentous green algae, such as, *Spirogyra neglecta*, *Pithophora oedogonia*, and *Cladophora calliceima*, have also shown good capacity for Cu(II) and Pb(II) sorption [116]. Dried biomass of *Oedogonium* sp. has shown enormous potential to sorb trace metals like Cu, Co, Cr, Fe, Hg, Ni, Zn and U in single and multi-ion solutions [10]. Some filamentous cyanobacteria, such as, *Phormidium valderianum* [66], *Oscillatoria* sp. [91], and *Spirulina platensis*, [7,43] also show excellent capacity to sorb heavy metals from aqueous solutions. Kumar et al. [72] have demonstrated great metal sorption capacity of five cyanobacterial mats dominated by species of *Oscillatoria*, *Phormidium*, *Lyngbya*, *Aulosira*, and *Scytonema*. A great apportionment of exopolysaccharides in the matrix of cyanobacterial mats is probably responsible for the binding of a large number of metal cations from the solution [71,73,75]. The biomass of cyanobacterial mats and filamentous algae, unlike that of microalgae, is easily harvestable for use in metal sorption process [13,72]. Filamentous algae [113,114] and cyanobacterial mats [70] also display better mechanical strength and reusability in comparison to other types of biosorbents.

The present review critically discusses the mechanisms of metal sorption by algae, importance of functional groups involved in metal binding, and the factors affecting metal sorption. It also discusses the significance of batch and continuous systems for metal sorption. Kinetic and isotherm modeling and breakthrough model prediction have also been emphasized.

2. Cellular sites and functional groups involved in metal binding

It has been very well established that metal ions bind to the cell surface and are also transported into the algal cell (Fig. 1). Whereas the former process does not depend on metabolic intervention, the latter is energy dependent requiring a number of metal transporters [16]. Many algae also have metabolism-driven metal efflux systems for maintaining their low intracellular concentration thereby avoiding metal toxicity. Metal ions inside the cell can be accumulated in cellular compartments, such as, vacuole and cell organelles [45,89]. Several biomolecules, such as, metallothioneins, phytochelatins, and polyphosphate bodies, also sequester metal ions from aqueous solutions [12,40,89,

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