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A comprehensive review on biosorption of heavy metals by algal biomass: Materials, performances, chemistry, and modeling simulation tools

Jinsong He, J. Paul Chen *

Department of Civil and Environmental Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore

HIGHLIGHTS

- Biosorption is a highly cost-effective technology for removal of heavy metals.
- Effective pretreatment approaches of biomass for better metal uptake are reviewed.
- Key functional groups of biosorbents and their roles in biosorption are described.
- Biosorption can be modelled by such reactions as ion-exchange and coordination.
- Biosorption kinetics can well be simulated by intraparticle diffusion models.

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ABSTRACT

Heavy metals contamination has become a global issue of concern due to their higher toxicities, nature of non-biodegradability, high capabilities in bioaccumulation in human body and food chain, and carcinogenicities to humans. A series of researches demonstrate that biosorption is a promising technology for removal of heavy metals from aqueous solutions. Algae serve as good biosorbents due to their abundance in seawater and fresh water, cost-effectiveness, reusability and high metal sorption capacities. This article provides a comprehensive review of recent findings on performances, applications and chemistry of algae (e.g., brown, green and red algae, modified algae and the derivatives) for sequestration of heavy metals. Biosorption kinetics and equilibrium models are reviewed. The mechanisms for biosorption are presented. Biosorption is a complicated process involving ion-exchange, complexation and coordination. Finally the theoretical simulation tools for biosorption equilibrium and kinetics are presented so that the readers can use them for further studies.

1. Introduction

Heavy metals pollution has become a global issue of great concern due to their higher toxicities, higher bioaccumulation in human body and food chain, nature of non-biodegradability, and most likely carcinogenicities to humans. Lead, mercury, chromium, arsenic, cadmium, zinc, copper and nickel are the most common contaminants found in contaminated surface water and groundwater as well as industrial wastewater. The occurrence of these heavy metals in water causes great threats to humans and other living organisms. Therefore, the World Health Organization (WHO), U.S. Environmental Protection Agency (USEPA) and many government environmental protection agencies have set the Maximum Contaminant Levels (MCLs) for the heavy metals in drinking water as well as trade effluent.

As heavy metals are non-biodegradable, clean-up of contaminated water and soil is rather challenging. It is greatly urgent to develop cost-effective technologies that can effectively remove them from contaminated water and soil as heavy metallic waste has been increasingly released to the natural environment in many places in the world. The currently practised technologies are precipitation, adsorption, reduction, coagulation, and membrane filtration. Their performances are normally acceptable; however, they have several drawbacks. In particular, they cannot work very well in treating heavy metals that have concentrations ranging from several to few hundred mg/L.

Biosorption is a sorption process, where biomaterial or biopolymer is engaged as sorbent. The phenomenon of biosorption was observed in early 1970s when the radioactive elements (also heavy

* Corresponding author. Tel.: +65 65168092.
E-mail addresses: paulchen@nus.edu.sg, jchen.enve97@gtalumni.org (J.P. Chen).

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metals) in the wastewater released from a nuclear power station were found to be concentrated by several algae. Early research conducted in laboratory studies had demonstrated that biosorption was a promising and cost-effective technology for the removal of heavy metals from aqueous solutions. Compared with such conventional methods as chemical reduction, ion exchange, precipitation, and membrane separation, biosorption technology possesses several advantages: low operating cost, high efficiency in detoxifying heavy metals that have lower concentrations, less amount of spent biosorbent for final disposal, and no nutrient requirements (Sheng et al., 2007).

A wide variety of active and inactive organisms have been employed as biosorbents to sequester heavy metal ions from aqueous solutions. It has been found that biosorbents are rich in organic ligands or the functional groups, which play a dominant role in removal of various heavy metal contaminants. The important functional groups are carboxyl, hydroxyl, sulfate, phosphate, and amine groups.

Many studies have shown the inactive (dead) biomass may be even more effective than active (living) one in removal of heavy metals. The inactive biomass requires neither food nor essential elements for biological growth, and may be available as waste or by-product. Over the past two decades, much effort had been devoted into identifying readily available non-living biomass capable of effectively removing heavy metals. These biosorbents typically include algae (Davis et al., 2003; Figueira et al., 2000), fungi (Gao et al., 2009), bacteria (Volesky and Holan, 1995), and agricultural waste (Sud et al., 2008). This review article mainly discusses the macro-algae and the derivatives from the theoretical and operation standpoints. However, it can also be applied to other types of biosorbents such as micro-algae and bacteria.

2. Biosorbents

2.1. Algal-based biosorbents

Among various biosorbents reported in the literature, marine algal biomass is identified as a promising biosorbent, in view of their high uptake capacities, low cost, renewability as well as the ready abundance of the biomass in many parts of the world's oceans. The global harvest of seaweeds for food and algal products (e.g., agar, alginate, and carrageenan) is over 3 million tons annually, with potential harvests estimated at 2.6 million tons for red algae and 16 million tons for brown algae (Chen, 2012).

Marine algae can be divided into several sub-groups according to the evolutionary pathways that are completely independent from one to another: "brown pathway" with brown algae (Phaeophyta), "red pathway" with red algae (Rhodophyta), and "green pathway" that includes green algae (Chlorophyta) along with mosses, ferns and several plants. The main differences among them lie in the cell wall, where biosorption occurs (Romera et al., 2007). The division of the marine algae summarized is given in Table 1 (Davis et al., 2003).

The cell walls of brown algae generally contain three components: cellulose (as structural support), alginic acid, polymers (e.g., mannuronic and guluronic acids) complexed with light metals such as sodium, potassium, magnesium and calcium, and polysaccharides (e.g., sulfated) (Romera et al., 2007). Alginic acid and some sulfated polysaccharides such as fucoidan are important components of the cell walls of brown algae (Phaeophyta). Alginates and sulfate are reportedly the predominant active groups in brown algae (Chen et al., 2002; Sheng et al., 2004). Green algae mainly have cellulose in the cell wall, and a high content of proteins is bonded to the polysacchatides. These compounds contain functional groups such as amino, carboxyl, sulfate, and hydroxyl, which play important roles in the biosorption. Red algae contain cellulose in the cell wall, but their biosorption capacities are attributed mainly to the presence of sulfated polysaccharides made of galactans.

Over the last two decades, the studies on biosorption were concentrated on the removal of heavy metals by brown algae (Davis et al., 2003, 2000; Figueira et al., 2000; Kleinübing et al., 2011; Lodeiro et al., 2005; Luna et al., 2010; Yu et al., 1999). The recent researches had been gradually devoted into the biosorption by green (Deng et al., 2009; Wan Maznah et al., 2012; Zakhama et al., 2011) and red algae (Ibrahim, 2011), and biopolymers derived from various biomaterials (Lim et al., 2008; Chen, 2012).

2.2. Biopolymer-based biosorbents

Biosorbents processed by simple approaches such as washing and drying of raw biomass described above could be used for sequestration of heavy metals. They have a major advantage of low cost as they are naturally available (e.g., seaweeds) and these simple approaches do not require chemical reagents and less manpower.

However, they have several disadvantages such as leaching of organic compounds during the operation. The total organic carbon (TOC) after heavy metal biosorption by raw seaweeds may reach as high as a few hundred ppm. In addition, the modification of the surfaces of these biosorbents for further removal of other contaminants is rather challenging. For example, seaweeds cannot effectively remove anionic contaminants from aqueous solutions. Alginate (a biopolymer) on the other hand can be modified chemically, and can efficiently remove anionic contaminants from water solutions. It can further be used to encapsulate other materials such as magnetite, leading to the formation of a multi-functional sorbent that has magnetic property and can remove both cationic heavy metal ions such as copper ions and anionic contaminants like arsenic (Lim et al., 2008).

3. Biosorption kinetics

The biosorption kinetics plays an important role in selection and design of reactor systems, as well as operations. Since heavy metal biosorption is metabolism-independent, it typically occurs rapidly, in particular for uptake of cationic metal ions.

Most of cationic metal uptake takes place within the first 20–60 min, followed by a relatively slow uptake process. The adsorption equilibrium for cationic heavy metal ions usually can be reached within 2–6 h (Ibrahim, 2011; Pavasant et al., 2006; Vijayaraghavan and Yun, 2008), which is much faster than activated carbons and metal oxide/hydroxide-typed adsorbents. Fig. 1 shows the typical adsorption kinetics when the *Sargassum* sp. was used (Chen and Yang, 2005).

However, biosorption for uptake of anionic contaminants (e.g., hexavalent chromium) is much lower than that of cationic contaminants. Typically, it would take more than half day to a few days to reach the biosorption equilibrium. For example, it was reported that the complete uptake of hexavalent chromium was achieved in 20 h when a chemically modified *Sargassum* sp. was used (Yang and Chen, 2008).

4. Biosorption equilibrium

Biosorption equilibrium is highly dependent upon the water chemistry, and the nature of heavy metal ions and the biosorbents. Higher cationic metal uptake occurs when pH is higher (e.g., above 4–6) as shown in Fig. 2a. However, better removal for anionic heavy ions can be obtained at lower pH. Ionic strength plays an