

Chapter 5

Heavy Metal Removal Through Biosorptive Pathways

Jinsheng Sun, Yulan Ji, Fang Cai, and Jing Li

5.1 Introduction

Rapid industrialization and urbanization have resulted in elevated levels of toxic heavy metals. This has been entangled, almost everywhere, in most industrial activities involving leakage and redistribution of heavy metals, such as mining and metalliferous smelting, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leatherworking, photography etc. Subsequently, these courses result in gradual exhaustion of metal and mineral resources. Especially, wastewaters produced from these industrial activities not only bring about serious environmental effect, but also threaten human health and ecosystem. These heavy metals, for the convenience of analyses, reportedly fall into three families, including toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.), precious metals (such as Pd, Pt, Ag, Au, Ru etc.), and radionuclides (such as U, Th, Ra, Am, etc.) [1].

Methods for removing metal ions from aqueous solution mainly consist of physical, chemical, and biological technologies. Traditional physiochemical methods include chemical precipitation, oxidation or reduction, filtration, ion exchange, electrochemical treatment, reverse osmosis, membrane technology, and evaporation recovery. Most of these are ineffective or excessively expensive when the metal concentrations are less than 100 mg/L [2, 3]. For example, usual physical pathways like ion exchange, activated carbon, and membrane adsorption belong to the latter costly group, especially when treating large amounts of wastewater. In recent years, in a way of financial convenience, applying biotechnology in controlling and

J. Sun (✉) • Y. Ji • F. Cai
School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072,
People's Republic of China
e-mail: jssun2006@vip.163.com

J. Li
Engineering Department, China Tianjin Chemical Engineering Design Institute,
No. 2 Gu Shan Road, Tianjin 300193, People's Republic of China

removing metal pollution has been paid much attention, and gradually becomes hot topic, for potential application, in the field of metal pollution control. Further alternative process is biosorption, which utilizes various certain natural materials of biological origin, including bacteria, fungi, yeast, algae, etc. These biosorbents possess instinctive metal-sequestering features to decrease the concentration of heavy metal ions in solution from ppm to ppb level. It can effectively capture dissolved metal ions and carry them out of dilute complex solutions with high efficiency and celerity; sound features as an ideal candidate for treating high volume and low concentration complex wastewaters [1].

This metabolism-independent mechanism is called biosorption [4]. According to Volesky and Holan [5], who presented an extensive review on biosorption, the strong biosorbent behavior of certain types of microbial biomass toward metallic ions is a function of the chemical makeup of microbial cells. In fact, the biomass in practice is nonliving and all cells are metabolically inactive. Compared with conventional treatment methods, biosorption has the following advantages [6–9]:

- High efficiency and selectivity for heavy metals in low concentrations
- Energy-saving
- Broad operational range of pH and temperature
- Easy reclamation of heavy metal
- Easy recycling of the biosorbent

Heavy metal removal by biosorption has been investigated during the last several decades [10]. The capability of some living microorganisms to accumulate metallic elements has first been observed from toxicological point of view [10]. However, further researches revealed that inactive/dead microbial biomass can passively bind metal ions via various physicochemical mechanisms. This discovery then led biosorption to the frontier of researches and an active field for the removal of metal ions. A large quantity of materials has been investigated as biosorbents for extensive removal of metals or organics. The tested biosorbents can be basically classified into the following categories: Bacteria (e.g., *Bacillus subtilis*), fungi (e.g., *Rhizopus arrhizus*), yeast (e.g., *Saccharomyces cerevisiae*), algae, industrial wastes (e.g., *S. cerevisiae* waste biomass from fermentation and food industry), agricultural wastes (e.g., corn core), and other polysaccharide materials, etc. [11]. The role of some groups of microorganisms has been given enough concern, such as bacteria, fungal, yeast, algae, etc.

Some potential biomaterials with high metal-binding capacity have been identified, such as *Sargassum natans*, *Bacillus subtilis*, *Rhizopus arrhizus*, *Saccharomyces cerevisiae*, and waste microbial biomass from the fermentation and food industries [5, 8, 9, 12–17]. Among these materials or biosorbents, some types bind and collect the majority of heavy metals with no specific priority, while others can even be specific for certain types of metals [5].

Researches on biosorption focus on the biosorbents, the biosorption mechanism, and large-scale experiments. Although many biological materials can bind heavy metals, only those with sufficiently high metal-binding capacity and selectivity for heavy metals are suitable for use in a full-scale biosorption process. Mechanisms

responsible for biosorption are understood to a limited extent, and commercial application of microbial biomass as a biosorbent suffered from problems associated with the physical characteristics of this material [18]. Attempts to apply biosorption process into practice have proved to be futile [19]. So, the biosorption process is basically at the stage of laboratory-scale study. Also, great efforts have to be made to improve biosorption process, including immobilization of biomaterials, improvement of regeneration and reuse, optimization of biosorption process, etc. In sum, theoretical and practical development about biosorption should be allowed to forge ahead.

The aim of this chapter is to present the state-of-the-art biosorbent investigation and to compare results found in the literature. The effects of environmental factors on biosorption capacities, biosorption mechanisms, advantages of biotechnology, regeneration/reuse of biosorbents, as well as proposals about improving biotechnology are presented and discussed. What is more, current hot topics, trends, and outlook of this field are also touched upon.

5.2 Brief Review of Physicochemical Removal Technology

Before the introduction, this brief review offers a control to the biological pathways that will be discussed in the next paragraph.

Conventional physicochemical methods, such as activated carbon, precipitation, reverse osmosis, membrane separation, chemical oxidation, and ionic exchange and so on, have been commonly used. However, most of those are less effective, excessively expensive, and eco-unfriendly when initial metal concentrations are in the range of 10–100 mg/L [20]. For instance, chemical precipitation and electrochemical treatment are not very effective, especially when metal ion concentration in aqueous solution is among 1–100 mg/L, and also produce large quantity of sludge required to treat with still more great difficulty [21].

The advantages and limitations in application of these traditional methods are given below in detail as follows:

5.2.1 Activated Carbon

It is a crude form of graphite with a random or amorphous structure, which is highly porous, exhibiting a broad range of pore sizes, from visible cracks, crevices, and slits of molecular dimensions [22]. And with its specific high surface area, microporous character, and chemical nature of their surface, activated carbons have made them potential adsorbents for the removal of heavy metals from industrial wastewater [23, 24]. In spite of its advantages, it also shows many shortcomings such as high cost to prepare, reactivation resulting in a loss of the carbon, performance type dependent of carbon, being nonselective, and so on. Although modified activated carbon [25] can improve the selectivity, its preparation cost roars up subsequently.

5.2.2 *Chemical Precipitation*

This pathway is widely used for heavy metal removal from inorganic effluent [26, 27]. Typically, the metal precipitates from the solution in the form of hydroxide [28]. Since lime or calcium hydroxide is the most commonly employed precipitant agent, this method gains availability at most corners of the world. Lime precipitation, another option, can be trusted to effectively treat inorganic effluent with a metal concentration of higher than 1,000 mg/L with a simple process. For instance, it helped to remove heavy metals such as Zn(II), Cd(II), and Mn(II) cations with initial metal concentrations of 450, 150, and 1,085 mg/L, respectively, in a batch continuous system [29]. In spite of its advantages, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge [30]. And generally it can hardly be used to handle low concentration of metal wastewater, which is below 100 mg/L [21]. Other drawbacks are its excessive sludge production that requires further treatment, the increasing cost of sludge disposal, slow metal precipitation, and the long-term environmental impacts of sludge disposal [31–33].

5.2.3 *Chemical Oxidation and Reduction*

Adding oxidizing or reducing agent makes toxic substances in wastewater being oxidized or reduced to nontoxic or low toxic substances. It has been reported that heavy metals such as Mn^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Cr^{3+} , and Hg^{2+} could be effectively removed using potassium ferrate(VI) as oxidation and co-precipitation [34, 35]. However, currently chemical oxidation and reduction was generally used as a pretreatment for wastewater before more powerful procedures.

5.2.4 *Membrane Separation*

Membrane separation methods like electrodialysis (ED), nanofiltration (NF), ultrafiltration (UF), and reverse osmosis (RO) [36] have received considerable attention for the treatment of inorganic effluent, since they are capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals [37–39]. Although it can be applied in occasions of low metal ion concentrations, for example, Tzanetakis's [40] removal efficiency of Co(II) and Ni(II) were 90% and 69%, at initial metal concentrations of 0.84 and 11.72 mg/L, respectively. The main disadvantages of these processes are inadequate selectivity, high energy consumption, and immature technologies, which limit the popularization of this technology.

5.2.5 Ion Exchange

This is a method that uses ion-exchange resin or agent to exchange ions in dilute solution to achieve the purpose of extraction or removal of certain ions in solution. And it is widely used for the recovery and removal of metals from process and waste streams in chemical process industries [41–43].

In general, ion exchange is reportedly effective to treat inorganic effluent within a relatively wide range of metal concentrations from 10 mg/L [44, 45] to 10–100 mg/L [46–48], or even up to higher than 100 mg/L [49, 50]. Furthermore, unlike chemical precipitation, ion exchange does not present any sludge disposal problems [51]. Despite these advantages, it also has some limitations in treating wastewater laden with heavy metals. Suitable ion exchange resins are not available for all heavy metals, and the capital and operational cost is high [52].

5.3 Biological Removal Technology

In recent decades, more and more attention have been paid to biotechnological removal of heavy metal and application of natural biological origin, including bacteria, fungi, yeast, algae, etc. These methods have the advantage over low operating cost, minimization of the pollutant concentration, and high efficiency in detoxifying the dilute effluents.

5.3.1 Heavy Metals Removal by Bacteria

5.3.1.1 Introduction

Novel methods of metal removal and recovery based on biological materials have been considered and widely used. Bacteria are the most abundant and versatile of microorganisms and constitute a significant fraction of the entire living terrestrial biomass of $\sim 10^{18}$ g [53]. In addition, because of their small size, ubiquity, ability to grow under controlled conditions, and resilience to a wide range of environmental situations, bacteria were often used to remove heavy metal ions [54]. Certain types of microbial biomass can retain relatively high quantities of metals on their cell wall due to its microstructure. Bacteria species such as *Bacillus*, *Pseudomonas*, *Streptomyces*, *Escherichia*, and *Micrococcus* have been tested for uptake metals or organics. Moreover, many factors such as biomass type and concentration, metal concentration, pH, and biomass–metal contact time affect removal ratios of heavy metals.

Table 5.1 summarizes some of the important results of metal biosorption using bacterial biomasses, according to published references [2, 11]. Metal uptake capacity does not necessarily reach the maximum values in the field application.

Table 5.1 Bacterial biomass used for metal removal

Metal ions	Bacteria species	Biosorption capacity (mg/g)	References
Pb	<i>Bacillus</i> sp.	92.3	[55]
	<i>Bacillus firmus</i>	467	[56]
	<i>Corynebacterium glutamicum</i>	567.7	[57]
	<i>Enterobacter</i> sp.	50.9	[58]
	<i>Pseudomonas aeruginosa</i>	79.5	[59]
	<i>Pseudomonas aeruginosa</i>	0.7	[60]
	<i>Pseudomonas putida</i>	270.4	[61]
	<i>Pseudomonas putida</i>	56.2	[62]
	<i>Streptomyces rimosus</i>	135.0	[63]
Zn	<i>Streptomyces rimosus</i>	30	[64]
	<i>Bacillus firmus</i>	418	[56]
	<i>Aphanothece halophytica</i>	133.0	[65]
	<i>Pseudomonas putida</i>	6.9	[62]
	<i>Pseudomonas putida</i>	17.7	[66]
	<i>Streptomyces rimosus</i>	30.0	[64]
	<i>Streptomyces rimosus</i>	80.0	[64]
	<i>Streptoverticillium cinnamomeum</i>	21.3	[67]
	<i>Thiobacillus ferrooxidans</i>	82.6	[68]
<i>Thiobacillus ferrooxidans</i>	172.4	[69]	
Cu	<i>Bacillus firmus</i>	381	[56]
	<i>Bacillus</i> sp.	16.3	[55]
	<i>Bacillus subtilis</i>	20.8	[70]
	<i>Enterobacter</i> sp.	32.5	[58]
	<i>Micrococcus luteus</i>	33.5	[70]
	<i>Pseudomonas aeruginosa</i>	23.1	[59]
	<i>Pseudomonas cepacia</i>	65.3	[71]
	<i>Pseudomonas putida</i>	6.6	[62]
	<i>Pseudomonas putida</i>	96.9	[61]
	<i>Pseudomonas putida</i>	15.8	[66]
	<i>Pseudomonas stutzeri</i>	22.9	[70]
	<i>Sphaerotilus natans</i>	60	[72]
	<i>Sphaerotilus natans</i>	5.4	[72]
	<i>Streptomyces coelicolor</i>	66.7	[73]
<i>Thiobacillus ferrooxidans</i>	39.8	[69]	
Cd	<i>Aeromonas caviae</i>	155.3	[74]
	<i>Enterobacter</i> sp.	46.2	[58]
	<i>Pseudomonas aeruginosa</i>	42.4	[59]
	<i>Pseudomonas putida</i>	8.0	[62]
	<i>Pseudomonas</i> sp.	278.0	[75]
	<i>Staphylococcus xylosus</i>	250.0	[75]
	<i>Streptomyces pimprina</i>	30.4	[76]
	<i>Streptomyces rimosus</i>	64.9	[77]

(continued)

Table 5.1 (continued)

Metal ions	Bacteria species	Biosorption capacity (mg/g)	References
Fe(III)	<i>Streptomyces rimosus</i>	122.0	[78]
Cr(IV)	<i>Bacillus coagulans</i>	39.9	[79]
	<i>Bacillus megaterium</i>	30.7	[79]
	<i>Zoogloea ramigera</i>	2	[80]
	<i>Aeromonas caviae</i>	284.4	[74]
	<i>Bacillus coagulans</i>	39.9	[79]
	<i>Bacillus licheniformis</i>	69.4	[81]
	<i>Bacillus megaterium</i>	30.7	[79]
	<i>Bacillus thuringiensis</i>	83.3	[82]
	<i>Pseudomonas</i> sp.	95.0	[75]
	<i>Staphylococcus xylosum</i>	143.0	[75]
Ni	<i>Bacillus thuringiensis</i>	45.9	[83]
	<i>Streptomyces rimosus</i>	32.6	[84]
Pd	<i>Desulfovibrio desulfuricans</i>	128.2	[85]
	<i>Desulfovibrio fructosivorans</i>	119.8	[85]
	<i>Desulfovibrio vulgaris</i>	106.3	[85]
Pt	<i>Desulfovibrio desulfuricans</i>	62.5	[85]
	<i>Desulfovibrio fructosivorans</i>	32.3	[85]
	<i>Desulfovibrio vulgaris</i>	40.1	[85]
U	<i>Arthrobacter nicotianae</i>	68.8	[86]
	<i>Bacillus licheniformis</i>	45.9	[86]
	<i>Bacillus megaterium</i>	37.8	[86]
	<i>Bacillus subtilis</i>	52.4	[86]
	<i>Corynebacterium equi</i>	21.4	[86]
	<i>Corynebacterium glutamicum</i>	5.9	[86]
	<i>Micrococcus luteus</i>	38.8	[86]
	<i>Nocardia erythropolis</i>	51.2	[86]
	<i>Zoogloea ramigera</i>	49.7	[86]
Th	<i>Arthrobacter nicotianae</i>	75.9	[86]
	<i>Bacillus licheniformis</i>	66.1	[86]
	<i>Bacillus megaterium</i>	74.0	[86]
	<i>Bacillus subtilis</i>	71.9	[86]
	<i>Corynebacterium equi</i>	46.9	[86]
	<i>Corynebacterium glutamicum</i>	36.2	[86]
	<i>Micrococcus luteus</i>	77.0	[86]
	<i>Zoogloea ramigera</i>	67.8	[86]

Some uptake values were experimentally observed, and some were predicted by the Langmuir model. Table 5.1 also provides the basic information to evaluate the possibility of using bacterial biomass for the removal of metal ions.

Large quantities of metals can be accumulated by a variety of processes dependent or independent on metabolism. Both living and dead biomass as well as cellular products such as polysaccharides can be used for this purpose. The basic principle of biosorption lies in biomass which are metabolically inactive [87].

Investigations from Ziagova et al. [75] proved that nonliving cells are advantageous over living counterparts for operating without an auxiliary cultivation system, immunity to toxic wastes around, and low storage requirement. A study [88] demonstrated that living and dead cells of *Bacillus sphaericus* OT4b31 showed a biosorption of 25% and 44.5% of Cr, respectively, while *B. sphaericus* IV(4)10 showed a biosorption of 32% and 45%, respectively. Practically biosorption experiments usually use heat-killed cells or bacterial biomass through heat treatment to break cell wall, exposing more functional groups, thus achieving maximum binding capacity [79, 89]. Biosorption is responsible for metal concentration by nonliving biomass owing to the absence of metabolic activity necessary for intracellular metal accumulation [90, 91].

5.3.1.2 Effect of Environmental Factors on Biosorption

Many researchers found that some environmental factors, such as pH, biomass concentration, metal concentration, and biomass-metal contact time, affected biosorption process, result in different removal effects. Further, the kinetics of adsorption has been examined and isotherms models, Langmuir and Freundlich, have been overwhelmingly used to analyze the equilibrium data.

Effect of pH

For biosorption of heavy metal ions, pH is one of the most important environmental factors. This value of solution strongly influences not only the site dissociation of the biomass surface, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation, speciation, and biosorption availability of the heavy metals [92]. Generally, at low pH values, several cytomembrane functional groups such as amine, phosphonate, sulfonate, carboxyl, and hydroxyl groups are probably associated with the hydrogen ions, making the overall surface charge on the microorganisms positive [93]. On the contrary, rising pH increases the negative charge at the surface of the cells until all relevant functional groups are deprotonated, which favors electrochemical attraction and adsorption of cations. However, when pH climbs to a certain value, for example, as high as 7.0, precipitation of the metal can occur by the formation of metal hydroxides [94]. The difference in optimum pH values may be attributed to the different components of the cell wall of these species. Reportedly, this optimum is organism dependent, due to different adsorptive sites of microorganisms [95]. For example, Ziagova et al. [75] observed that optimum pH values were estimated to be 1.0 for *Staphylococcus xylosus* with 36% biosorption yield and between 4.0 and 5.0 for *Pseudomonas* sp. with 42% biosorption yield in the case of chromium which exists in the solution as anionic group. They revealed that *S. xylosus* is a Gram positive bacterium with its surface consisting of peptidoglycans, teichoic, and teichuronic acids. These substances provide most of the anionic groups of

the cell and are protonated at low pH and facilitate the interaction of chromium. Also, the study of Hancock [96] indicated that the optimum pH value for chromium biosorption was estimated to be 4.0. However, Gialamouidis [87] demonstrated that this value for Mn(II) biosorption was 6.0 for both of *Pseudomonas* sp. and *S. xylosus*, which suggested that the adsorption of metals onto the biomass could be ruled by ionic attraction.

Effect of Biomass Concentration

Most studies reported that high biomass concentrations result in low metal sorption due to electrostatic interactions between cells, which protect binding sites from metal occupation [97]. However, increase of the biomass concentration results in reducing the equilibrium concentration of metal solution owing to the fact that there are more available sites for interaction on biomass. The study of Gialamouidis et al. [87] showed that the biosorption capacity of metal ions is inversely proportional to biomass concentration, when the initial concentration of metal ions is kept constant with *Pseudomonas* sp. concentrations over 4.0 g/L. Ziagova et al. [75] observed that chromium removal with *Pseudomonas* sp. does not change significantly at higher than 1.0 g/L biomass concentrations. However, in the case of chromium, there is a significant increase in the metal uptake around 40% by altering biomass concentration of *S. xylosus* from 1.0 to 8.0 g/L. This may be attributed to the higher number of available binding sites, which interact with chromium ions of the solution, as it has been reported before [98, 99]. At higher than 8.0 g/L biomass concentration, there is no further positive effect on chromium removal, which probably results from limitations in metal ion mobility.

Effect of Contact Time

The kinetics of metal uptake, assumed to be a passive physical adsorption at the cell surface, is very rapid and occurs in a very short time after the microorganisms have come into contact with metal ions [100]. The adsorption speed of uranium by *Citrobacter freundii* was very fast in the first 20 min and then slowed down gradually and reached equilibrium after 50 min [101]. In the study of Ziagova et al. [75], the amount of adsorbed Cd(II) reached the highest value, 50%, within the first 30 min with *Pseudomonas* sp. and 55% after 1.0 h with *S. xylosus*., respectively. Gialamouidis et al. [87] indicated that the biosorption capacities of *Pseudomonas* sp. and *S. xylosus* for Mn²⁺ increased with contact time rapidly and thereafter it proceeded at a lower rate and finally attained equilibrium within 10 min. This result is important because equilibrium time is one of the parameters for economical wastewater treatment plant application [24]. This behavior suggests that in the initial stage adsorption takes place rapidly on the external surface of the adsorbent followed by a slower internal diffusion process, which may be the rate-determining step.

5.3.1.3 Biosorption Models

Kinetics Model

In order to examine the mechanism of biosorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to describe the data. The linear pseudo-first-order equation is given as follows [102]:

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2.303}t \quad (5.1)$$

where q_t and q_{eq} are the amounts of metal ions adsorbed at time t and equilibrium (mg/g), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}).

The linear pseudo-second-order equation is given [102]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}}t \quad (5.2)$$

where k_2 is the equilibrium rate constant of pseudo-second-order biosorption (g/mg min).

These results of Gialamouidis et al. [87] strongly suggest that the biosorption of Mn(II) onto *Pseudomonas* sp. and *S. xylosus* cells is most appropriately represented by a pseudo-second-order rate process. In the study of Xie et al. [101], the adsorption kinetics of uranium by *C. freudii* showed that the pseudo-second-order model fitted the adsorption curve much better than the pseudo-first-order model, which indicated the adsorption rate was proportional to the number of unoccupied sites. Song et al. [103] demonstrated that the equilibrium of Au(III) biosorption was achieved within 5 min and the adsorption yield reached 100%, whereas that of Cu(II) was only 66.61% after 30 min in the binary system of Au(III) and Cu(II) by magnetotactic bacteria. They suggested that the first-order equation of Lagergren in most cases does not fit well for the whole range of contact time [104]. The pseudo-second-order equation can be used in this case assuming that the measured concentrations are equal to cell surface concentrations, and it is more likely to predict behavior over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step. Consequently, they demonstrated that the experimental data were fitted well into the pseudo-second-order kinetic model in the single and binary component situations.

Isotherm Models

Langmuir and Freundlich isotherm equations were frequently used to describe the equilibrium state for single-ion adsorption experiments. The theoretical basis of Langmuir equation relies on the assumption. That is, there is a finite number of

Table 5.2 Adsorption isotherm parameters in the different conditions

Metal ions	Bacteria species	Langmuir constants			Freundlich constants			References
		Q_{\max} (mg/g)	$b \times 10^{-3}$ (L/mg)	R^2	K_f (L/g)	$1/n$	R^2	
Cd	<i>Paedomonas</i> sp.	278	9	0.901	9.08	0.531	0.998	[75]
	<i>S. xylosus</i>	250	8	0.912	7.00	0.547	0.996	[75]
	<i>Ochrobactrum anthropi</i>	37.3	37	0.971	44.64	2.45	0.961	[107]
Cr	<i>Pseudomonas</i> sp.	95	7	0.949	1.42	0.676	0.997	[75]
	<i>S. xylosus</i>	143	5	0.967	1.33	0.758	0.974	[75]
	<i>Ochrobactrum anthropi</i>	86.2	6	0.932	2.45	1.60	0.981	[107]
Au	<i>Magnetotactic bacteria</i>	37.7	978	0.9939	27.56	0.0637	0.9901	[103]
Cu	<i>Magnetotactic bacteria</i>	36.8	160.5	0.9985	16.09	0.091	0.9428	[103]
	<i>Ochrobactrum anthropi</i>	32.6	52	0.991	3.00	1.72	0.816	[107]
Mn	<i>Pseudomonas</i> sp.	109	13	0.99	4.30	0.536	0.93	[87]
	<i>S. xylosus</i>	59	26	0.97	3.22	0.533	0.99	[87]

binding sites which are homogeneously distributed over the adsorbent surface of the cells, having the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules. The mathematical description of the equation is considered.

$$Q = \frac{Q_{\max} b C_i}{1 + b C_i} \quad (5.3)$$

where C_i is the metal residual concentration in solution (mg/L); Q_{\max} is the maximum specific uptake corresponding to sites saturation (mg/g), and b is the biomass-metal binding affinity (mg/L) [105].

The Freundlich equation is the empirical relationship whereby it is assumed that the adsorption energy of a metal binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. This empirical equation is presented.

$$Q = K_f \cdot (C_i)^{1/n} \quad (5.4)$$

where K_f and n are constants indicating adsorption capacity and adsorption intensity, respectively [106]. The results of some studies about Langmuir and Freundlich isotherm models are presented in Table 5.2.

5.3.1.4 Selective Adsorption in the Case of Multicomponent System

Competitive biosorption takes place in the multicomponent system. Under most conditions, aqueous sources of precious metals contain not only one but also several kinds of metal ions. Although many published reports are available on the single-metal biosorption, limited attention has been paid to the biosorption of multimetal

Table 5.3 The Freundlich parameters and the correlation coefficients

$C_{0, \text{other metal}}/\text{mg/L}$	Au(III) ions			Cu(II) ions		
	K_F	n	R^2	K_F	n	R^2
0	27.56	15.6985	0.9901	16.09	11.0254	0.9428
80	44.33	22.8833	0.9265	1.27	5.1125	0.9693
320	38.64	10.2669	0.9214	0.04	1.4656	0.9857

Note: $C_{0, \text{other metal}}$ represents the other metal concentration in solution. When $C_{0, \text{other metal}} = 0$, it is single ion solution; when not, it is binary system

Table 5.4 The Langmuir parameters and the correlation coefficients

$C_{0, \text{other metal}}/\text{mg L}^{-1}$	Au(III) ions			Cu(II) ions		
	Q^0 (mg/g)	b (L/mg)	R^2	Q^0 (mg/g)	b (L/mg)	R^2
0	37.7	0.9780	0.9939	36.8	0.1605	0.9985
80	48.8	4.1000	1.0000	22.4	0.0046	0.9260
320	47.6	5.2500	1.0000	27.7	0.0007	0.9026

Note: The meaning of $C_{0, \text{other metal}}$ is the same as Table 5.3

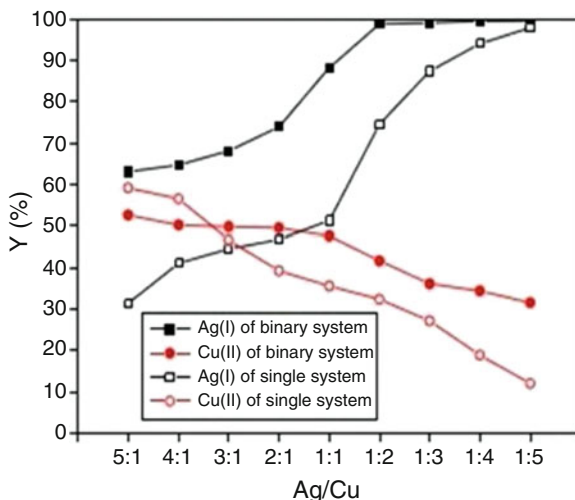
ion system [108]. Summarization of these present literatures concerning biosorption of this more complicated system revealed different biosorptive features from those of single counterparts [103]. To make this reasonable, competition among the different metal ions for the cellular surface binding sites is believed to certainly occur and depend to some extent on the ionic characteristics for certain microbe. The examination of the effects of binary metal ions in various combinations, discussed in this section, is more representative of the actual environmental problems as it has been also reported [109], since real wastewaters are polluted with more than one toxic metals.

Song et al. [103] observed that the maximum adsorption capacity for Au(III) by magnetotactic bacteria in Au-Cu binary system was nearly doubled as that in the single system. The results demonstrated that Cu(II) has a “catalyzing” effect on Au(III) sorption during competitive biosorption process, which also indicates that the MTB cell walls have high selectivity toward Au(III) ions in binary-solute biosorption process.

Besides, Langmuir model and Freundlich model have been also introduced to describe both single and binary system biosorption. The Freundlich and Langmuir constants evaluated from linear regression analysis are listed in Tables 5.3 and 5.4, respectively. Within the metal concentration range of 80–500 mg/L, both models were suitable for describing the adsorption isotherms of Au(III) or Cu(II) ions; that of Au(III) was more fitted by Langmuir model and that of Cu(II) by Freundlich in binary system.

In the study of Wang et al. [108], simultaneous biosorptions of Ag(I) and Cu(II) ions by *Magnetospirillum gryphiswaldense* (MSR-1) were evaluated using several mediums that contained 2 mmol/L each of the two metal ions. In each medium, the molar ratios of Ag(I) and Cu(II) were different, which were 5:1, 4:1, 3:1, 2:1, 1:1,

Fig. 5.1 The results of Ag(I)–Cu(II) binary system adsorption experiments (Reprinted from Ref. [108]. With kind permission of © Elsevier BV (2011))



1:2, 1:3, 1:4, 1:5. The results were compared with that of single systems, which included the same molar concentration of Ag(I) and Cu(II).

As shown in Fig. 5.1, the biosorption capacities of Ag(I) on MSR-1 in the presence of Cu(II) were higher than that of noncompetitive conditions. Interestingly, when the molar ratios of Ag(I) and Cu(II) were less than 4:1, the biosorption capacities of Cu(II) on MSR-1 were higher than that of noncompetitive cases, whereas those were lower under the molar ratios of Ag(I) to Cu(II) of both 5:1 and 4:1. They deduced that the most possible factor which affected the phenomenon of selective biosorption was the ions themselves.

In addition, they demonstrated that the adsorption isotherm of Ag(I) can also be perfectly expressed by the Langmuir model just as that in the single ion solution. Nevertheless, both models are mathematically unsuitable for describing Cu(II) adsorption isotherms in binary system, with the regression coefficients (R^2) less than 0.95. So, a new mathematically consistent Eq. (5) was selected for accurate description of Cu(II).

$$q_e = a(1 + be^{-kC_e}) \quad (5.5)$$

The constants in this case evaluated from regression analysis were $a = 3.50917$, $b = 7.38993$, $k = 0.11474$, with a high regression coefficient (R^2) 0.99343. This model, not fit for the single metal system in this study, is under further checking among vast analogous competitive adsorptive systems to find universality before it is introduced to mathematically describe the prohibited one(s). Undoubtedly, it has an important guiding significance for the future research.

The results indicated that biosorption in binary mixtures is a rather complicated adsorption mechanism affected by a lot of factors, including surface charge,

functional groups, properties of the solution (e.g., pH), and the adsorbates (e.g., concentration, ionic strength, and weight). In addition, there are many interactions not only between the metal ions but also between the metal ions and the surface of the biomass [75]. If highly selective biosorbents for a certain metal ion were created, great progress would be made in the removal of heavy metal ions.

5.3.1.5 Regeneration of Biosorbents

The entire biosorption process for metal removal include sorption followed by desorption, i.e., to concentrate the solute. Biotechnological exploitation of biosorption technology for removal of heavy metal(s) depends on the efficiency of the regeneration of biosorbent after metal desorption. It is important to reclaim the biosorbents especially, since the biomass preparation is costly. Therefore, nondestructive recovery by mild and cheap desorbing agents is desirable for regeneration of biomass and reuse in multiple cycles. Appropriate eluants are necessary to attain the above-mentioned objective, which strongly depends on the type of biosorbent and the mechanism of biosorption [21]. Also, the eluant must meet the following requirements: (1) Non-damaging to the biomass, (2) less costly, (3) environmental friendly, and (4) effective [11]. Acidic and alkaline condition were used for desorption. The eluants such as CaCl_2 with HCl, HCl with EDTA, NaOH were reported [11]. According to the study of Chen et al. [110], approximately 74.8% of the adsorbed Cu was desorbed from nonliving *Pseudomonas putida* CZ1 by 1.0 M CH_3COOK , and more than 80% Zn. Gialamouidis et al. [87] observed that more than 88% of Mn(II) adsorbed by *Pseudomonas* sp. was released into the HNO_3 solution at the first cycle. After three cycles, biosorption ability of *Pseudomonas* sp. reduced by 77.4%, which may be due to the fact that HNO_3 solution modifies the cell wall, while the desorption ability remains to high levels.

The efficiency of desorption is often expressed by the S/L ratio, i.e. solid to liquid ratio. The solid represents the solid sorbent (in mg dry wt) and the liquid represents the amount of eluant applied (in mL). High values of S/L are desirable for complete elution and to make the process more economical. Sometimes, metal-selective elution is desirable and it is dependent on metal sequestration mechanism. Dilute mineral acids, EDTA, carbonates and bicarbonates, NH_4OH , KHCO_3 , and KCN have been used to remove metal(s) from the loaded biomass [111].

To date, less attention has been paid to investigate the regeneration ability of the biosorbent, more relevant work is necessary for future field biosorption application.

5.3.1.6 Biosorption Mechanism Discussion

One of them is bioaccumulation, based on the incorporation of metals inside the living biomass. Another process is biosorption, in which metallic ions remain at the cellular surface by different mechanisms [11]. Elucidation of mechanisms active in

metal biosorption is essential for successful exploitation of the phenomenon and for regeneration of biosorbent materials in multiple reuse cycles. The complex nature of biosorbent materials makes this task particularly challenging [5]. These results show that in binary mixtures, biosorption is a rather complicated adsorption mechanism affected by a lot of factors, including surface charge, functional groups, properties of the solution (e.g., pH), and the adsorbates (e.g., concentration, ionic strength, and weight). In addition, there are many interactions, not only between the metal ions, but also between the metal ions and the surface of the biomass. Velásquez and Dussan [88] suggested that in dead cells metals could have been adhered to surface molecules such as the S-layer which is a porous one that can have saturation velocity. Metallic ions must find a union target and pass through other cellular components before this happens. What is more, in living cells cellular density increases as time elapses; therefore, there are more available binding sites for metals. Additionally, if the metal gets inside the cell, it first needs to join surface molecules and then gets in through different mechanisms. So, S-layer proteins might execute a trapping role of metallic ions in both living and dead cells, being a potential alternative for bioremediation processes of heavy metals in field. Algae, fungi, yeast, and bacteria can remove heavy metals from aqueous solutions by binding the cationic metals onto negatively charged functional groups distributed on their cell walls, such as carboxyl and phosphoryl groups [112, 113]. According to Volesky and Holan [5], who presented an extensive review on biosorption, the strong biosorbent behavior of certain types of microbial biomass toward metallic ions is a function of the chemical makeup of microbial cells. Beveridge [114] reported that bacteria are excellent biosorbents due to their high surface-to-volume ratios and high content of potentially active chemisorptions sites such as teichoic acid in their cell walls. The study of Gialamouidis et al. [87] is very interesting. They calculated thermodynamic parameters such as enthalpy change (ΔH_o), entropy change (ΔS_o), and free energy change of the sorption (ΔG_o), demonstrating that the heats of biosorption of Mn(II) on *Pseudomonas* sp. and *S. xylosus* cells were found to be of the same order as the heat of chemisorptions whereas the heat of biosorption on *Blakeslea trispora* cells is lower and in the range of physical adsorption. Besides, equilibrium between the cell surface and the metal ions is usually rapidly attained and easily reversible, because the energy requirements are limited. Studies of copper or zinc interactions with microorganisms showed that Cu or Zn may be associated with the functional groups on the cellular surface [115–118], intercellular accumulation, and storage via active cationic transport systems [114, 119], or precipitation of Cu sulfides at the biofilm surface [120]. In terms of biosorption, polysaccharides, proteins, and lipids on bacterial cell walls offer many functional groups such as carboxylate, hydroxyl, phosphate, amine, and sulphate groups which can bind metal ions. This natural affinity of biological compounds for metallic elements could contribute to the purification of metal-contaminated wastewater [18]. Vullo et al. [18] thought that metal biosorption depends upon the available surface negative charges. Metal ions biosorption could affect these surface negative charges and thus bacterial electric properties. Electrophoretic mobility measurements are generally done to understand bacterial cell electric properties [121–123], determining Zeta potential values.

Moreover, in their study, for concentrations greater than 0.05 mM, no changes are observed in Z potential, which could be explained by the saturation of the cell surface sites available for Cd. Xie et al. [101] observed that the adsorption capacity of uranium by *C. freudii* increased after the strain was pretreated with 0.5 mol/L NaOH. Proteins, lipids, and some dissolved polysaccharides on the surface of the bacteria could be removed by NaOH. The macromolecular configuration of the cell wall was destroyed and became relaxed, which could improve the diffusion capability and facilitate the entry of metal ions into the cell. In addition, acetyl in testa could be removed by alkali, and amidocyanogen could be exposed to form Louis alkali, which increased the active sites and the adsorption capacity eventually. By sequential pretreatment with NaOH and methanol-thick hydrochloric acid, the carboxyl on the *C. freudii* walls was locked and the adsorption capacity of uranium decreased by 45.66% compared with raw bacterium strain, which confirmed that carboxyl, as one of the active sites, played an important role in adsorption.

It is necessary to continue searching for the most promising biosorbents from an extremely large pool of readily available and inexpensive biomaterials [8, 9]. The mechanism involved in metal biosorption is far from well understood up to date. It is our mission to investigate the microbe-metal interactions and obtain the mechanism of metal uptake by biosorbents.

Bacteria may either possess the capacity for biosorption of many elements or, alternatively, depending on the species, may be element specific. It is likely that, in the future, microorganisms will be tailored for a specific element or a group of elements, using recombinant DNA technology which is based on genetic modification using endorestrictive nucleases [53].

5.3.2 Heavy Metals Removal by Fungi

5.3.2.1 Introduction

Powered by another mechanism, fungi also reveal the feature of metal capturers. There are three groups of fungi that have major practical importance: molds, yeasts, and mushrooms. Filamentous fungi and yeasts have been investigated for biosorption of heavy metal ions in many instances.

It is known for a long time that metallic ions are important to fungal metabolism. The presence of heavy metals had a significant impact on not only the metabolic activities of fungal cultures, but also the commercial fermentation processes. The results from these studies led to a notion of using fungi for the removal of toxic metals from wastewater and recovery of precious metals from process waters [124]. Fungal cell walls are mainly 80–90% polysaccharide, with proteins, lipids, polyphosphates, and inorganic ions, making up the wall-cementing matrix [21]. It is because of these components that both living and dead fungal cells have an extraordinary ability for taking up toxic and precious metals.

The biosorption of heavy metal by filamentous fungi and yeast have been reported and reviewed in many articles. The fungal organisms are widely used in a variety of large-scale industrial fermentation processes. For example, strains of *Aspergillus* are used in the production of ferrichrome, kojic acid, gallic acid, itaconic acid, citric acid, and enzymes like amylases, glucose isomerase, pectinase, lipases, and glucanases while *Saccharomyces cerevisiae* in the food and beverage industries. The use of fungi biomass as an adsorbent for heavy-metal pollution control not only can generate economic benefits by recycling industries wastes, but also reduce the burden of disposal costs associated with the waste biomass produced. Alternatively, the biomass can also be grown using unsophisticated fermentation techniques and inexpensive growth media [125].

This section will review and summarize the removal of heavy metals by yeast (*Saccharomyces* spp.) and filamentous fungi (such as *Penicillium* sp., *Aspergillus* sp., *Mucor* sp., *Rhizopus* sp.) from aqueous solutions.

5.3.2.2 Fungal Biosorbents

Research has proved that yeast and filamentous fungi can remove toxic metals, recover precious metals, and clean radionuclides from aqueous solutions to various extents. Yeasts of genera *Saccharomyces*, *Candida*, different species of *Penicillium*, under some circumstances, as well as *Aspergillus* are efficient biosorbents for heavy metal ions. Table 5.5 summarizes some of the important results of metal biosorption using fungal biomass.

Except for these four kinds of fungal biomass widely covered by the published reports, there are also a lot of other fungi employed for the same purpose.

The cell wall of *R. arrhizus* involves a high content of chitin. The ability of chitin to complex metal ions has been confirmed [148]. Viable *R. arrhizus* could remove Cu(II) with the maximum specific uptake capacity of 10.76 mg/g at 75 mg/L, the initial Cu(II) concentration [148]. Of the six species of inactivated fungal mycelia, *R. arrhizus*, *Mucor racemosus*, *Mycotypha africana*, *Aspergillus nidulans*, *A. niger*, and *Schizosaccharomyces pombe*, *R. arrhizus* exhibited the highest capacity ($q_{\max} = 213 \mu\text{mol/g}$). Further experiments with different cellular fractions of *R. arrhizus* showed that Zn was predominantly bound to cell-wall chitin and chitosan ($q_{\max} = 312 \mu\text{mol/g}$). *R. arrhizus* were reported to adsorb Th(IV) [152], Pb(II) [153], Cd(II), Ni(II), and Cr(III) [154]. Brady and Tobin [155] investigated the freeze-dried *R. arrhizus* biomass for its potential to absorb the hard metal ion Sr^{2+} and the borderline metal ions Mn^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} , and Pb^{2+} from aqueous solutions.

Biosorption of metal ions such as Li^+ , Ag^+ , Pb^{2+} , Cd^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Sr^{2+} , Fe^{2+} , Fe^{3+} , and Al^{3+} by *Rhizopus nigricans* biomass was studied, with the maximum biosorption capacity for the individual metal ions ranging from 160 to 460 $\mu\text{mol/g}$ [156].

Table 5.5 Fungal biomasses for removal of heavy metals from aqueous solution

Biosorbents	Metal ions	Biosorption capacity(mg/g)	References
<i>Saccharomyces cerevisiae</i>	Pb	270.3	[126–129]
	Ni	46.3	[127, 129]
	Cr	32.6	[127, 128]
	Cd	31.75	[128–130]
	Cu	6.35	[128, 129]
	Zn	35.31	[128, 129]
	Hg	64.19	[129]
	Co	24.75	[129]
	Fe	16.8	[131]
	Ag	59	[131]
	Pd	40.6	[132]
	Pt	44.0	[133]
	U	180	[131]
	Th	63	[134]
<i>Candida albicans, Candida utilis</i>	Pb	833.33	[135]
	Cu	23	[136, 139]
	Cr	7	[137, 139]
	Zn	28	[139]
	Cd	19	[139]
<i>Candida tropicalis</i>	Pb	39	[139]
	Zr	179	[138]
<i>Penicillium chrysogenum</i>	Pb	55	[140]
	Cd	56	[141]
	Ni	260	[142]
	Cu	92	[140]
<i>Penicillium simplicissimum</i>	Cd	52.5	[143]
	Zn	65.5	[143]
	Pb	76.9	[143]
	Cu	112.3	[144]
<i>Penicillium purpurogenum</i>	As	35.6	[145]
	Hg	70.4	[145]
	Cd	110.4	[145]
	Pb	252.8	[145]
<i>Penicillium canescens</i>	As	26.4	[146]
	Hg	54.8	[146]
	Cd	102.7	[146]
	Pb	213.2	[146]
<i>Penicillium digitatum</i>	Cd	3.5	[15]
	Pb	5.5	[15]
<i>Penicillium griseofulvum</i>	Cu	1.51	[147]
<i>Penicillium italicum</i>	Cu	2	[2]
	Zn	0.2	[2]
<i>Penicillium notatum</i>	Cu	80	[125]
	Zn	23	[125]
	Cd	5.0	[125]

(continued)

Table 5.5 (continued)

Biosorbents	Metal ions	Biosorption capacity(mg/g)	References
<i>Penicillium janthinellum</i>	U	52.7	[125]
<i>Aspergillus niger</i>	Cu	9.53	[148]
	Cd	3.43	[149]
	Pb	7.24	[149]
	Ni	0.96	[149]
	Cu	180	[150]
<i>Aspergillus terreus</i>	Fe	164.5	[151]
	Cr	96.5	[151]
	Ni	19.6	[151]
	Cu	224	[151]

The live and dead white rot fungus *Trametes versicolor* entrapped in Ca-alginate beads were able to adsorb Cd(II). The maximum experimental biosorption capacity was 102.3 ± 3.2 and 120.6 ± 3.8 mg/g, respectively [157].

A white rot fungus species *Lentinus sajorcaju* biomass was entrapped into alginate gel via a liquid curing method in the presence of Ca(II) ions. The maximum experimental biosorption capacity for entrapped live and dead fungal mycelia of *L. sajorcaju* were found to be 104.8 ± 2.7 mg/g and 123.5 ± 4.3 mg/g, individually [158].

5.3.2.3 Influencing Factors of Removal of Heavy Metals by Fungi

Pretreatment

The study of Yunsong Zhang et al. [159] showed that ethanol/caustic pretreatment could increase the biosorption capabilities of Cu^{2+} on *Saccharomyces cerevisiae*. In addition, SEM and Zeta potential of the three samples account for that caustic and ethanol-pretreatment resulted in the change of baker's yeast surface structure and charge which is relative to adsorption. These results demonstrate that the increase of biosorption capacity for Cu^{2+} by ethanol and caustic-baker's yeast was attributed to the increase and exposure of carboxyl and amino groups on the surface of biomass sample.

Biosorption of chromium ions was found to vary with the type of pretreatment. All pretreatment methods (acid (0.1N H_2SO_4); alkali (0.01N NaOH); acetone (50%, v/v); formaldehyde (10%, v/v); cetyl trimethyl ammonium bromide (CTAB) (5%, w/v); polyethylemine (PEI) (1%, w/v); and 3-(2-amino ethyl amino) propyl trimethoxy silane (APTS) (3%, v/v)) increased the biosorption of chromium compared to the autoclaved *A. niger* biomass [160]. Park et al. [161] also reported approximately 30% removal of chromium using *A. niger* biomass. The acetone pretreated biomass showed a biosorption capacity of 1.8 mg/g, which was slightly higher compared to autoclaved biomass.

pH

Solution's initial pH is a critical parameter for adsorption experiments [162]. This parameter strongly influences the solution chemistry of the metals, the activity of functional groups (carboxylate, phosphate and amino groups) on the cell wall, as well as the competition of metallic ions for the binding site [1]. At low pH (<1.0), the biosorption capacity for metal ions is very low, because large quantity of hydrogen ions competes with metal ions at sorption sites. As the pH increases, more negatively charged cell surface become available thus facilitating great metal uptake [163]. However, metal precipitates at high pH values (>7.0) thus inhibiting the contact of metal with the most fungal biomass.

Ting Fan et al. [143] investigated the effects of the initial pH on biosorption of Cd(II), Zn(II), and Pb(II) ions in aqueous solution by *Penicillium simplicissimum*. Maximum biosorption capacities were obtained at pH 4.0, 6.0, and 5.0 for Cd(II), Zn(II), and Pb(II), respectively.

The biosorption of nickel(II) ions by deactivated protonated yeast was observed with respect to the initial pH by V. Padmavathy et al. [164]. The adsorption capacity was pH dependent with a maximum value of 11.4 mg/g at a pH of 6.75. The cadmium(II) ion adsorption capacity of Baker's yeast increased with increasing pH, and was maximum at a pH of 6.5 [165].

Contact Time

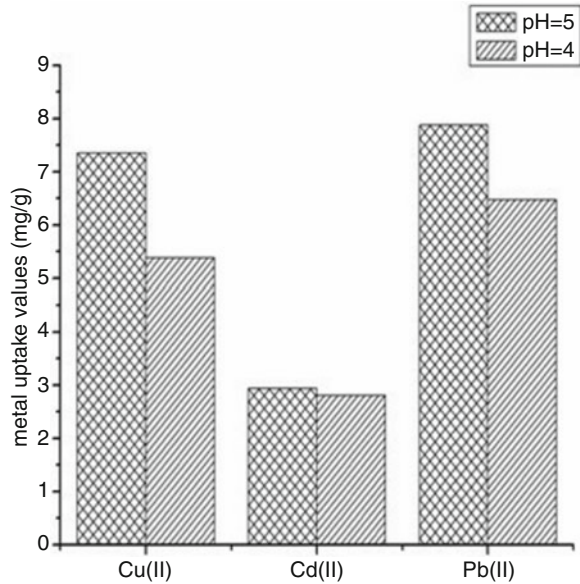
It is reported that biosorption of chromium consisted of two phases [161]: a primary rapid phase and a secondary slow phase. The rapid phase lasted for about 15 min and accounted for a major portion in the total metal biosorption. Chromium removal of 72% was observed in this rapid phase. A maximum chromium removal of 76% was achieved after 2 h. From 2 h to the end of the kinetic study (12 h), biosorption was slow and chromium removal varied by $\pm 2\%$. This rapid initial uptake is consistent with reports on the biosorption of Cr(VI) by other researchers [166–170].

This is because the kinetics of metal adsorption is usually rapid during the early period of contact between the adsorbent and adsorbate possibly by reason of electrostatic attraction. The active adsorption sites of the adsorbent become involved in metal complexation as soon as the adsorbent is introduced into the system. It has been suggested that the slow second phase of metal ions uptake may be due to the reduced availability of active sites [171].

Initial Metal Ion Concentration

As a rule, increasing the initial metal concentration results in an increase in the biosorption capacity because the initial metal concentration provides a driving force to overcome mass transfer resistances between the biosorbent and biosorption

Fig. 5.2 Competitive metal uptake values (Reprinted from Ref. [103]. With kind permission of © Elsevier (2007))



medium so that higher sorption capacities were obtained at higher initial concentrations. The adsorption yields are determined at different initial metal ion concentrations. Increasing the metal ion concentration generally caused a decrease in the biosorption yield. In the case of lower concentrations, the ratio of initial number of metal ions to the available sorption sites was low and higher biosorption yields were obtained. At higher concentrations, the available sites of biosorption became fewer and the saturation of the sorption sites was observed. So biosorption yields decreased.

The effect of initial metal ion concentration on the biosorption capacity of *Aspergillus flavus* was studied by Tamer Akar and Sibel Tunali [172]. The biosorption of Pb(II) and Cu(II) ions on *A. flavus* increased with increasing initial concentration of metal ions, becoming saturated at 200 and 150 mg/L for Pb(II) and Cu(II) ions, respectively.

5.3.2.4 Selectivity and Competitive Biosorption by Fungi

Competitive biosorption of Cd^{2+} and Pb^{2+} together with Cu^{2+} ions with ethanol treated yeast cells were conducted for solution containing 25 mg/L of each metal ions at pH 4 and 5 [130]. In their study [130], the highest biosorption capacity of Cu^{2+} ions was determined with caustic treated waste baker's yeast cells; but for comparison, ethanol treated yeast biomass was also used for biosorption of Cu^{2+} ions in competitive biosorption studies. The competitive metal uptake values are shown in Fig. 5.2.

The competitive biosorption capacities of the yeast biomass for most metal ions were lower than non-competitive conditions. The decreased metal uptake in competitive conditions was thought to be a response to increased competition between like charged species for binding sites of the ethanol treated yeast cells. The order of the sorption capacity was found as $Pb > Cu > Cd$ for both pH values.

P. canescens at competitive or noncompetitive cases exhibited the same preferential order: $Pb(II) > Cd(II) > Hg(II) > As(III)$. Under noncompetitive conditions, the sorption capacity was 26.4 mg/g for As(III), 54.8 mg/g for Hg(II), 102.7 mg/g for Cd(II), and 213.2 mg/g for Pb(II) respectively. The competitive adsorption capacity for the heavy metal ions were 2.0 mg/g for As(III), 5.8 mg/g for Hg(II), 11.7 mg/g for Cd(II), and 32.1 mg/g for Pb(II), when the initial concentration of the metal ions was 50 mg/L [146].

The biosorption capacities of *Penicillium simplicissimum* in the binary and ternary metal mixture of Cd(II) + Zn(II), Zn(II) + Pb(II), and Cd(II) + Zn(II) + Pb(II) system were lower than noncompetitive conditions that of unitary system of Cd(II), Zn(II), Pb(II), and Cd(II) [143]. The results clearly demonstrated that the combined action of multiple ions was antagonistic and that Cd(II) exerted the inhibitory effect on the biosorption of other metals, followed by Pb(II) and Zn(II).

A similar phenomenon had been observed in the binary adsorption Pb(II) and Cu(II) biosorption onto *Aspergillus flavus*, where it was shown that Pb(II) and Cu(II) strongly competed with each other; the biosorption capacities of the binary metal mixture were lower than that of noncompetitive conditions; and the uptake capacities of Pb(II) ions were smaller influence than Cu(II) ions [172].

All these published experiments illustrated prohibited competitive biosorptive capacities, in comparison with the non-competitive cases, for the biomass to uptake metal ions. The most likely reason for this antagonistic effect is the competition for adsorption sites on the cell surfaces and/or the screening effect by the competing metal ions.

5.3.2.5 Mechanism of Metal Uptake

DAI Shu-juan et al. [173] provided that cadmium can be adsorbed from electroplating wastewater by waste *Saccharomyces cerevisiae* and accumulated mainly in form of chemical chelating. Electrostatic attraction, hydrogen bonding, and van der Waals force all function in adsorption process. And $-NH_2-$, $-C=O-$, $-C=O-NH-$, $-CH_3$, $-OH$ are the main adsorption groups.

Fourier transform, infrared, and X-ray photoelectron spectroscopies were used to discover that carboxyl, amide, and hydroxyl groups on the biomass surface were involved in the sorption of copper and cadmium by *Penicillium chrysogenum* and ion exchange and complexation dominated the sorption process [174].

The understanding of the mechanism by which microorganisms accumulate metals is crucial to the development of microbial processes for concentration, removal, and recovery of metals from aqueous solution. Metabolism-independent

metal binding to the cell walls and external surfaces is the only mechanism present in the case of non-living biomass. Metabolism-independent uptake essentially involves adsorption process such as ionic, chemical, and physical adsorption. A variety of ligands located on the fungal walls are known to be involved in metal chelation. These include carboxyl, amine, hydroxyl, phosphate, and sulfhydryl groups. Metal ions could be absorbed by complexing with negatively charged reaction sites on the cell surface [175, 176]. The relative importance of each functional group is often difficult to resolve [177]. Microbial cell wall is rich in polysaccharide and glycoproteins such as glucans, chitin, mannans, and phospho-mannans. These polymers form abundant source of metal binding ligands. Cell walls of fungi present a multi-laminate architecture where up to 90% of their dry mass consists of amino or non-amino polysaccharides [178]. In general, the fungal cell wall can be regarded as a two-phase system consisting of the chitin skeleton framework embedded in an amorphous polysaccharide matrix [178]. Up to 30% of *Aspergillus niger* biomass is comprised of an association of chitin and glucan [179]. Chitin and chitosan components of the cell wall are suggested to be important for metal uptake [180, 181].

5.3.2.6 Modeling of Biosorption: Isotherm and Kinetic Models

Analysis of equilibrium data is important for developing an equation that can be used for design purposes. There are several isotherm and kinetic models to describe the sorption phenomena.

Isotherm Modeling

The biosorption isotherms by biomasses are usually described by the well-known adsorption isotherm models of Freundlich and Langmuir (see Sect. 5.3.1.3).

The parameters of Langmuir and Freundlich isotherm model are presented in Table 5.6. Broadly speaking, most of the data were fit better to Langmuir isotherm model than Freundlich isotherm model.

Except for these two models, Redlich–Peterson and Temkin adsorption isotherms were also used to describe the sorption phenomena. Arzu Y. Dursun [183] used Langmuir, Freundlich, and Redlich–Peterson adsorption models to describe the sorption phenomena of Cu(II) and Pb(II) to dried *A. niger*. In view of the results, the isotherms appeared to follow the Langmuir model more closely than the other models at all the temperatures studied. However, the Freundlich and Redlich–Peterson adsorption models also seemed to agree well with the experimental data considering that percentage error values were lower than 11.5. Jing-song Wang [184] used Langmuir, Freundlich, and Temkin isotherms models to describe the sorption phenomena of U(VI) to *A. fumigatus*. Based on the correlation coefficient R^2 , the Langmuir isotherm model was the best model to describe the experimental data, but the negative value of q_{max} indicated that this model is not suitable for

Table 5.6 Adsorption isotherm parameters

Metal ions	Bacteria species	Langmuir constants			Freundlich constants			References
		Q_{\max} (mg/g)	$b \times 10^{-3}$ (L/mg)	R^2	K_F	n	R^2	
Pb	<i>Candida albicans</i>	828.5	60.0	0.995	51.309	4.716	0.935	[135]
	<i>Penicillium simplicissimum</i>	144.9	590	0.999	33.0	3.27	0.9016	[144]
Cr	<i>Aspergillus niger</i>	3.98	1.1	0.95	2.57	6.6	0.95	[149]
Ni	<i>Aspergillus niger</i>	2.2	140	0.98	1.47	1.79	0.98	[149]
Cd	<i>Aspergillus niger</i>	18.08	20	0.997	6.26	4.4	0.671	[182]
Cu	<i>Saccharomyces cerevisiae</i>	10.27	15.13	0.9968	0.4048	1.762	0.9644	[159]
	<i>Penicillium simplicissimum</i>	106.4	193	0.9978	19.3	3.02	0.9102	[144]
Zn	<i>Aspergillus niger</i>	26.1	120	0.998	6.95	3.6	0.770	[182]

this case. Compared with the other two models, it is clear that both the Freundlich and Temkin isotherm models fitted with the experimental data well, and the former model was a better fit than the latter.

Kinetic Modeling

The biosorption kinetics by biomasses is usually described by first-order rate equation and the second-order rate equation (see Sect. 5.3.1.3).

In most cases, the first-order equation of Lagergren does not fit well over the entire adsorption period and is generally applicable for the initial 30–50 min of the sorption process [185]. Different to the pseudo first-order model, the pseudo-second-order model predicts the behavior over the whole duration of adsorption and is in agreement with the feature of the adsorption mechanism in the rate-controlling step.

Kuber C. Bhainsa et al. [186] investigated the kinetic of biosorption for Th by *Aspergillus fumigatus*. Data obtained from the kinetic of uptake when modeled with pseudo-second-order equation showed excellent fitting and the kinetic rate constant and R^2 values are >0.99 . This suggests that the kinetics of Th uptake followed Lagergren's pseudo-second-order equation. This was also further confirmed by calculating the q_e based on pseudo-second-order reaction that showed very good fit between the experimental data and the predicted curve obtained by modeling the uptake value.

Removal of cadmium and zinc ions from aqueous solution by living *Aspergillus niger* was investigated by LIU Yun-guo et al. [182]. The parameters of pseudo-first and pseudo-second order rate kinetics are presented. The theoretical Q_{eq} values estimated from the first-order kinetic give significantly different values compared with the experimental values, and the correlation coefficients are also found to be slightly lower. The correlation coefficients for the second-order kinetic model and the theoretical values of Q , also agree well with the experimental ones.

Almost all of the kinetic data of sorption by fungi biomass kinetic were more fitted to pseudo-second-order equation.

5.3.3 Heavy Metals Removal by Algae

5.3.3.1 Introduction

Algae, primarily marine microalgae, 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 [187, 188]. Actually a vast array of biological materials, especially bacteria, yeasts, fungi, and algae have received increasing attention for heavy metal removal and recovery due to their good performance, low cost, and large available quantities. In general, the heavy metal uptake capacities varied significantly for different types of biomass studied. For divalent heavy metal ions, the reported values for bacterium biomass typically ranged from 0.05 to 0.2 mmol/g, fungi and yeast 0.2–0.5 mmol/g, fresh water algae 0.5–1.0 mmol/g, and marine algae 1.0–1.5 mmol/g [189].

From the published literature, among the three groups of algae (red, green, brown algae) brown algae received the most attention. Higher uptake capacity has been found for brown algae than for red and green algae [190]. Table 5.7 summarized the results achieved with brown algae, green algae, and red algae. We know that brown algae have since proven to be the most effective and promising substrates among other biosorbents.

The development of new biosorbent materials is a research area full of challenge, as algae biomass is an accessible, economically competitive, and renewable source. Therefore, its potential value in the treatment of heavy metal wastewater is obvious.

5.3.3.2 Influencing Factors on Biosorption

Effect of pH

This parameter plays an important role for the biosorption process of heavy metal ions from aqueous solution, according to a variety of earlier studies [192–194]. Whereas the calculation from the solubility product equilibrium constant (K_{sp}) [195] demonstrated that the suitable pH ranges for the various metal ions were slightly different, i.e., experiments for Cu^{2+} sorption was performed for the pH range of 1–6, Cd^{2+} at pH of 1–8, Zn^{2+} at pH of 1–7, and Pb^{2+} at pH of 1–7.5. For the algae biosorption, pH is also a key factor. Algal biomasses contain high content of carboxyl groups from mannuronic and guluronic acids on the cell wall polysaccharides, which suggests that the biosorption process could be affected by changes in the solution pH [196]. Some examples are cited of algae biosorption on different metal ions.

Table 5.7 Uptake of metals by algal biomass

Metal ions	Algae	q_{\max} (mmol/g)
Cd	<i>Ascophyllum nodosum</i> (B)	0.338–1.913
	<i>Chaetomorha linum</i> (G)	0.48
	<i>Chlorella vulgaris</i> (G)	0.30
	<i>Codium fragile</i> (G)	0.0827
	<i>Corallina officinalis</i> (R)	0.2642
	<i>Fucus vesiculosus</i> (B)	0.649
	<i>Gracilaria edulis</i> (R)	0.24
	<i>Gracilaria Salicornia</i> (R)	0.16
	<i>Padina</i> sp.(B)	0.53
	<i>Padina tetrastomatica</i>	0.53
	<i>Porphira columbina</i> (R)	0.4048
	<i>Sargassum</i> sp. (B)	1.40
	<i>Sargassum baccularia</i> (B)	0.74
	<i>Sargassum natans</i> (B)	1.174
	<i>Sargassum siliquosum</i> (M)	0.73
Ni	<i>Ascophyllum nodosum</i>	1.346–2.316
	<i>Chlorella miniata</i>	0.237
	<i>Chlorella vulgaris</i>	0.205–1.017
	<i>Chondrus crispus</i> (R)	0.443
	<i>Codium taylori</i> (G)	0.099
	<i>Fucus vesiculosus</i>	0.392
	<i>Galaxaura marginata</i> (R)	0.187
	<i>Padina gymnospora</i> (B)	0.170
	<i>Sargassum fluitans</i> (B)	0.409
	<i>Sargassum natans</i>	0.409
	<i>Sargassum vulgare</i> (M)	0.085
	<i>Scenedesmus obliquus</i>	0.5145
Pb	<i>Ascophyllum nodosum</i>	1.313–2.307
	<i>Chlorella vulgaris</i>	0.47
	<i>Cladophora glomerata</i> (G)	0.355
	<i>Chondrus crispus</i>	0.941
	<i>Codium taylori</i>	1.815
	<i>Fucus vesiculosus</i>	1.105–2.896
	<i>Galaxaura marginata</i>	0.121
	<i>Gracilaria corticata</i> (R)	0.2017–0.2605
	<i>Padina gymnospora</i>	0.314
	<i>Padina tetrastomatica</i> (B)	1.049
	<i>Polysiphonia violacea</i> (R)	0.4923
	<i>Sargassum fluitans</i>	1.594
	<i>Sargassum hystrix</i> (B)	1.3755
	<i>Sargassum natans</i>	1.1487–1.221
	<i>Sargassum vulgare</i>	1.100
<i>Ulva lactuca</i> (G)	0.61	
<i>Undaria pinnatifida</i> (B)	1.945	

(continued)

Table 5.7 (continued)

Metal ions	Algae	q_{\max} (mmol/g)
Cu	<i>Chlorella miniata</i> (G)	0.366
	<i>Chlorella vulgaris</i>	0.254–0.758
	<i>Sargassum</i> sp.	1.08
	<i>Scenedesmus obliquus</i> (G)	0.524
Zn	<i>Chlorella vulgaris</i>	0.37
Cr(VI)	<i>Chlorella vulgaris</i>	0.534–1.525
	<i>Sargassum</i> sp.	1.30–1.3257
	<i>Scenedesmus obliquus</i>	1.131
Fe(III)	<i>Chlorella vulgaris</i>	0.439

Source [191]

(B) Brown alga, (G) Green alga (R) Red alga

Experimental biosorption on green algae *Spirogyra* species studied by V. K. Gupta [197, 198] showed that the percent adsorption of Cr(VI) increases with pH from pH 1.0 to 2.0 and thereafter decreases with further increase in pH. And the maximum adsorption at all the concentrations takes place at pH 2.0. As to lead sorption, when the pH of the lead solution (100 and 200 mg/L) increased from 2.99 to 7.04, the adsorption capacity of lead was changed, i.e., it first increased from pH 2.99 to pH 5.0 and then dramatically decreased up to pH 7.04. The results stated strong pH dependence of biosorption. This is consistent with the results obtained for the other adsorbent systems [199, 200].

Additionally, cadmium (II) uptake by *C. vulgaris* studied by Z. Aksu [185] is also a function of solution pH. The results showed that the biosorption of cadmium (II) increased with pH up to 4.0 and then declined with further increase in pH. And the maximum equilibrium uptake value was found to be 62.3 mg/g at pH 4.0.

Summarizing, almost all the relative publications revealed similar information that a good control of pH is of great significance for metal biosorption by algae.

Effect of Temperature

The binding of most metals to microorganisms by biosorption observed to enhance as temperature rising [201–203]. Also, increasing temperature is known to stir up the diffusion rate of adsorbate molecules within pores as a result of decreasing solution viscosity and will also modify the equilibrium capacity of the adsorbent for a particular adsorbate [204]. Thus temperature is also an important factor affecting the adsorption.

Research of cadmium (II) and nickel (II) biosorption with *C. vulgaris* carried out by Z. Aksu [185, 208] manifested that the equilibrium uptake of cadmium (II) and nickel (II) ions to the dried green alga was significantly affected by the temperature. The uptake of cadmium (II) decreased with an increasing temperature, while nickel (II) increased. And their optimum adsorption temperature was 20°C and 45°C, respectively. That is, cadmium (II) adsorption is normally exothermic; thus, the extent

of adsorption generally increases with decreasing temperature. This result is typical for biosorption of metals involving no energy-mediated reactions, where metal removal from solution is due to purely physical/chemical interactions between the biomass and metal in solution. Increasing the temperature reduced the biosorption capacity of biomass. Nevertheless, nickel (II) adsorption was endothermic; thus, the extent of adsorption increased with increasing temperature. Besides, the sorption of nickel (II) ions by dried *C. vulgaris* may involve not only physical but also chemical sorption. So at higher temperatures, an increase in active sites occurs due to bond rupture.

There are many studies that show the information on the effect of temperature in recent years, which are associated with the adsorption mechanism [196, 198, 206].

Effect of Contact Time

The contact time has also been evaluated as one of the most important factors affecting the biosorption efficiency. The alga *Chlorella vulgaris* was reported to exhibit the feature of rapid uptake of nickel and then reach the equilibrium in 30–60 min [205]. Also, the study of Sari A. [196] showed the biosorption efficiency of Cd (II) ions by *C. virgatum*. The biosorption efficiency increases with rising contact time up to 60 min, after which it is almost constant. Another biosorption of lead from aqueous solutions by green algae (*Spirogyra* sp.) [198] demonstrated that maximum adsorption took place within first 100 min. In fact, the equilibrium time needed for the different metal–biomass systems reportedly range from 1 to 3 h, that is, about 90% of the total metal ion sorption was achieved within 60 min [207].

Overall, reported experiments on contact time reveal, without exception, that the sorption took place in two stages: A very rapid surface adsorption followed by a long period of equilibrium. Adsorption got slowed down in the later stage because initially a large number of vacant surface sites may be available for adsorption and after a certain point of time, the remaining vacant surface sites may be difficult to occupy due to forces between the solute molecules of the solid and bulk phase [208–210]. The diminishing removal with increasing time may also attribute to intraparticle diffusion process dominating over adsorption [211].

Effect of Biomass Dosage

The amount of biosorbent used for the treatment of heavy metals is also an important parameter which influences the biosorption capacity. The biosorption of Cu(II) in the work of Karthikeyan [212] showed an increased uptake of Cu(II) with the alga quantity which can be accounted for the higher dose of adsorbent in the solution and the greater availability of exchangeable sites for the ions. But the maximum uptake was attained at about 100 mg. And he analyzed that this trend was caused by the formation of biosorbent aggregates at higher biomass concentration, which

in turn could reduce the effective surface area available for the biosorption. In fact, many studies [196, 198, 213] showed the similar phenomenon that with increasing biomass dosage, the absorption efficiency experienced an inverted-U curve arousal.

5.3.3.3 Adsorption Mechanism

Metal ion binding during biosorption processes has been found to involve complex mechanisms, such as ion-exchange, complexation, electrostatic attraction, and microprecipitation [5]. In fact, for many years, it had been thought that in the process of biosorption, metal ions bind to highly developed surface of a biosorbent via the mechanism of physical adsorption [214]. Whereas the biosorption of Cr^{3+} , Cd^{2+} , and Cu^{2+} ions by blue-green algae *Spirulina* sp. studied by Chojnacka [215] showed that the mechanism of biosorption is rather chemisorptions than physical adsorption (ion-exchange), which was further confirmed by the low surface area associated with physical adsorption and the presence of cations that appeared in the solution after biosorption. The maximum contribution of physical adsorption in the overall biosorption process was evaluated to be 3.7%. Study of the mechanisms of biosorption by Raize [216] manifested that the main cadmium cation sequestration mechanism by the algal biomass was apparently chelation, while that of nickel was mainly ion exchange. Lead cations exhibit higher affinity to the algal biomass, and their binding mechanism includes a combination of ion exchange, chelation, and reduction reactions, accompanied by metallic lead precipitation on the cell wall matrix. The SEM method was used by Han et al. [217] to probe that the surface complexation was the exact mechanism in Cr(III) biosorption by *Chlorella miniata*. In fact, among various proposed mechanisms, ion exchange was thought to be the most important process for the algal biomass [214]. Ion exchange mechanism was thought to be reversible, and more than 90% of the biosorbed metal could be recovered through acid washing [9].

5.3.3.4 Biosorption Models

Isotherm Modeling

The equilibrium data, commonly known as adsorption isotherms, are the basic requirements for the design of the adsorption systems. Several isotherm equations, such as Langmuir, Freundlich, Redlich–Peterson, D-R isotherms, and so on, have been used for the equilibrium modeling of biosorption systems. Langmuir and Freundlich isotherms (see Sect. 5.3.1.3) were widely used to quantitatively describe metal sorption by algae [196, 198, 205, 206, 218–220].

Additionally, some authors explain that Langmuir isotherm corresponds to a dominant ion-exchange mechanism while the Freundlich isotherm shows adsorption–complexation reactions taking place in the adsorption process

Table 5.8 Langmuir and Freundlich parameters for the sorption of the test metals by the selected algae

Algae	Metal ion	Langmuir constant			Freundlich constant		
		q_{\max} (mg/g)	b (L/mg)	R^2	K_F (mg ¹⁻ⁿ /g l ⁿ)	n	R^2
<i>Spirogyra neglecta</i>	Cu	40.83	0.034	0.96	5.44	0.370	0.89
	Cd	27.95	0.047	0.97	5.01	0.320	0.89
	Zn	31.51	0.034	0.99	4.23	0.368	0.94
	Ni	26.30	0.042	0.99	4.27	0.366	0.92
	Pb ²⁺	90.19	0.015	0.97	4.75	0.513	0.92
<i>Pithophora oedogonia</i>	Cu	23.08	0.069	0.98	5.72	0.265	0.92
	Cd	13.07	0.038	0.98	2.02	0.344	0.93
	Zn	8.98	0.103	0.99	2.98	0.214	0.94
	Ni	11.81	0.039	0.98	1.84	0.342	0.95
	Pb ²⁺	71.13	0.020	0.96	5.28	0.461	0.91
<i>Cladophora calliceima</i>	Cu	14.08	0.088	0.98	4.26	0.229	0.92
	Cd	9.14	0.098	0.97	2.95	0.218	0.92
	Zn	8.51	0.101	0.98	2.80	0.216	0.95
	Ni	7.67	0.074	0.99	2.00	0.257	0.94
	Pb ²⁺	40.50	0.022	0.94	5.29	0.414	0.88
<i>Hydrodictyon reticulatum</i>	Cu	8.72	0.103	0.96	2.81	0.221	0.98
	Cd	7.20	0.071	0.97	1.83	0.262	0.98
	Zn	3.70	0.115	0.92	1.26	0.212	0.99
	Ni	13.86	0.021	0.99	1.14	0.444	0.96
	Pb ²⁺	24.00	0.054	0.97	4.87	0.299	0.90
<i>Aulosira fertilissima</i>	Cu	21.77	0.060	0.99	4.83	0.285	0.92
	Cd	14.57	0.087	0.98	4.28	0.236	0.92
	Zn	19.15	0.049	0.99	3.63	0.310	0.93
	Ni	4.16	0.235	0.83	2.05	0.145	0.99
	Pb ²⁺	31.12	0.042	0.97	4.99	0.338	0.89

[221, 222]. Furthermore, most of the equilibrium data were fit better to Langmuir isotherm model than Freundlich isotherm model. The parameters of Langmuir and Freundlich isotherm model are presented in Table 5.8 [223].

Kinetic Models

In order to investigate the mechanism of biosorption and potential rate-controlling step such as mass transport and chemical reaction processes, kinetic models are used to test the experimental data. Numerous models (e.g., Elovich, diffusion, pseudo-first-order, and pseudo-second-order equations) have been suggested to analyze the kinetics of sorption process. Kinetic models based on the capacity of the adsorbent such as the first-order equation and second-order expression were commonly used (see Sect. 5.3.1.3).

In the work of O.M. Freitas [224], experimental data suggested that the pseudo-first-order model successfully describes the kinetics of the biosorption of Zn on *L. hyperborea* and Cd on *B. bifurcate*. The results of Aravindhyan Rathinam [28] also suggest that kinetics of cadmium biosorption by *H. valentiae* biomass followed pseudo-first-order kinetic model very well.

The pseudo-second-order kinetic model has been applied successfully to metal biosorption by several algae [185, 198, 200, 206, 225–228]. Additionally, these parameters in equations can change depending on experimental conditions as it was found by P. Lodeiro [225].

The Weber and Morris sorption kinetic model [229], a kind of diffusion model, was employed to investigate the sorption mechanism in the study of Prasert Pavasant [195].

To sum up, kinetic model is an important part of the study of heavy metal biosorption, from which we can get the information of the control steps and mechanism of the process.

5.3.4 Plant Leaves and Their Extraction

5.3.4.1 Introduction

There is a considerable potential for adopting a natural, abundant, and economical metal adsorption system, and plant leaves and their extraction, which are cheap and easily available in a great supply, could be used as an adsorbent for the removal of heavy metals from aqueous solution. In fact, tree leaves and their extraction are frequently employed in heavy metal removal [230–236]. Studies show that adsorption capability also relies on leaves used. Examples of efficient types of plant leaves for removal of metal ions are reed [237] for cadmium, poplar for lead and copper [238, 239], cinchona for copper [239], pine for nickel [240], and cypress for aluminum [241]. Moreover, R. Salim [232] conducted cadmium removal experiments from aqueous solutions by 20 species of plant leaves and their combinations. The results showed that most efficient types of plant leaves for cadmium removal were those of styrax, plum, pomegranate, and walnut.

5.3.4.2 Effects of Environmental Factors on Biosorption

Effect of pH

The pH of the sorbate solution is considered one of the most important environmental factors affecting the biosorption process. This factor is capable of influencing not only the binding site dissociation state, but also the solution chemistry of the target metal [242]. Successful biosorption of base metal cations usually takes place in the range of pH 3–7, and is extremely pH dependent. Özer A. and Özer D. [243]

reported an optimal pH value for lead and nickel uptake of 5.0, while Vianna LNL [244] found that maximal copper, cadmium, and zinc uptakes happened at pH 4.5, and decreased significantly when the pH was dropped to 3.5 or 2.5.

H. Benaissa [231] studied the removal of copper by dried sunflower leaves finding the maximum copper sorption occurs at around initial pH 5–6. A. Sharma and K.G. Bhattacharyya [230] used leaf powder as biosorbent to reclaim Cd (II) obtaining continuous adsorption increases from 8.8% at pH 4.0 to 70.0% at pH 7.0, and 93.6% at pH 9.5. Similarly, R. Salim [232] found that the optimum experimental condition reached at pH 4.1. Rice bran was also used for the removal of Cr (VI) from wastewater [245] and the maximum removal yield was 99.4% also at a low pH of 2.0. Even grape stalks wastes came in handy to absorb copper and nickel ions and I. Villaescusa [246] found a pH-dependent profile for the course. Maximum sorption for both metals was found to occur at around pH 5.5–6.0. Y. Bulut and Z. Baysal [247] used wheat bran as a sorbate on biosorption of Pb (II) and found that the Pb (II) adsorption by wheat bran increases with pH. It can be observed that the removal of Cu (II) and Pb (II) exhibits similar trend, i.e., it increases with increasing pH, climbing to maximum at a certain pH range. Bin Yu and Y. Zhang [248] reported that the maximum removal of Pb (II) by sawdust sorption occurs around pH 5.0, while that of Cu (II) 7.0. Furthermore, the greatest increases in the sorption rate of metal ions on sawdust were observed in a range of pH from 2 to 8 for copper and 2–5 for lead.

Effect of Temperature

As one of the factors affecting the biosorption efficiency, temperature was studied in many papers [249–253]. S. Qaiser [254] studied the biosorption of lead from aqueous solution by *Ficus religiosa* leaves and found that the temperature change in the range of 20–40 °C affected the biosorption capacity and the maximum removal was observed at 25 °C. In M.S. Al-Masri's [255] study, the influence of temperature on U, Pb, and Cd removal capacities using different parts of poplar trees is different. The maximum U and Cd removal capacity using leaves occurred at a temperature of 25 °C while the maximum U, Pb, and Cd removal capacities using branches occurred at a temperature of 35 °C.

5.3.4.3 Mechanism Analysis

The mechanism of metal biosorption varies with the metal species and type of biosorbent [217]. To bind and accumulate these pollutants, different previously mentioned mechanisms reportedly also empower the course, solo or ensemble, such as physical adsorption, complexation, ion exchange, and surface microprecipitation [203, 256–258]. For example, S. Qaiser [254] reported the release of Ca, Mg, and Na ions during lead biosorption revealing ion exchange as the suitable major

removal mechanism. Javad Zolgharnein [259] in his study of Cr (VI) adsorption onto *Elaeagnus* tree leaves found chemisorption as the predominant mechanism of this special biosorption.

5.3.5 Summary

In fact, 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. And biosorption is an alternative process, which provides a variety of sorption materials, including bacteria, fungi, yeast, algae, plant leaves, etc. stated above. These biosorbents with relatively high metal-binding capacity and selectivity possess metal-sequestering property and are suitable for the extraction of metal ions from large volumes of water. Therefore it is an ideal candidate for the treatment of high-volume and low concentration complex wastewaters.

5.4 Combination and Improvement of Different Pathways

Commercial application of microbial biomass as a biosorbent may suffer from the problem of how to remove or condense the metal ions-loaded microorganisms from aqueous solution to facilitate reclaiming in the next step. Generally, millipore filtration and evaporation methods have been carried out, but the high cost of membrane and high energy consumption impede them from wide application. Song et al. [103] studied competitive biosorption of Au(III) and Cu(II) ions by magnetotactic bacteria, which may be significant for developing promising biosorbents. Besides, Wang et al. [108] observed that Cu (II) promoted the adsorption of Ag (I) in the competitive biosorption of Ag (I) and Cu (II) on *Magnetospirillum gryphiswaldense* (MSR-1), which was confirmed magnetotactic bacterium [260], was reported to be sensitive to magnetic field and might be one of the promising options for solving this problem by means of external field. These bacteria were observed to be able to move along the local magnetic field lines, which is a very useful feature to facilitate them to be easily separated from the solutions. This unique finding indicates the high possibility to recover heavy metal ions from wastewater using the method of “MTB biosorption and magnetic separation”, which was simple, effective, and environmentally friendly. However, it is still faced with another problem. For example, Song et al. [261] applied a magnetotactic bacterium, *Stenotrophomonas* sp., to remove Au(III) from contaminated wastewater. The analyses from FTIR and XRD confirmed that the reduction of Au(III) to Au(0) by the reductants on the MTB biomass occurred, and the deposition of nanocrystal Au(0) particles, ranging from 24.7 to 31.4 nm, could be estimated on the biomass surface. Although easy

to remove the MTB-nano Au(0) group by the external magnetic field, it may be a great challenge to separate MTB from nano Au(0), because both nano Au(0) and nanometer-scale magnetosomes own magnetism.

Also, according to combination of abiotic and biotic components, Chen et al. [110] used the bacteria-mineral composite as a geochemically reactive solid and quantified its trace metal ion scavenging ability. In their study, the first quantitative comparison of the metal-binding capacities of *P. putida* CZ1–goethite composite to its individual components was evaluated. As a consequence, the nonliving cells–goethite composite retained approximately 82% more Zn than that predicted by its solo counterpart.

What is more, some attention was focused on immobilization technology for heavy metal removal biomaterial [262–265]. Entrapment, cellular aggregation, and surface fixation are the most common methods to support this technology [266–270]. The choice of an adequate matrix for cell immobilization affects the process performance, since the metal biosorption efficiency can be affected by these heterogeneous systems [271, 272]. Microorganisms loaded natural and synthetic adsorbents have also been used for separation and preconcentration of heavy metals at trace levels. *S. cerevisiae* loaded on sepiolite was utilized as biosorbent for copper(II), zinc(II), and cadmium(II) in natural waters [264]. Bag et al. [91] proposed a biosorptive enrichment procedure for Cr (III) and Cr (VI) ions by *Saccharomyces cerevisiae*-loaded sepiolite. *S. cerevisiae* and *Chlorella vulgaris* loaded on silica gel has been used for the separation–preconcentration of Pt^{2+} and Pd^{2+} [273]. Vullo et al. [18] made another progress by successfully immobilizing *P. veronii* 2E on inert surfaces such as Teflon membranes, silicone rubber, and polyurethane foams. In addition, *P. veronii* 2E was found to be able to grow on all three surfaces and develop a film over the matrix surfaces, form aggregates, and adhere to glass during batch cultures. Removal rate of Pb(II) reaches the summit 97.7% at pH 4, at 200 mg/L of initial Pb(II) concentration with 10 g/L of *P. sanguineus* beads, prepared by dropping a mixture of 1.5% (w/v) sodium alginate solution and *P. sanguineus* mycelial mat into a 2% (w/v) CaCl_2 solution [274].

Furthermore, the idea about combination of abiotic and biotic components coupled with the immobilization theory and magnetic separation technology. Magnetic particles have been applied as a new sorbent to adsorb metal ions, in which the difficulty of separation was resolved in an external magnetic field [275]. Based on these researches, the biofunctional magnetic bead was synthesized and utilized in the wastewater treatment [276]. Li et al. [276] removed heavy metal in wastewater by bio-functional magnetic beads constituted by the powder of *Rhizopus cohnii* and Fe_3O_4 particles coated with alginate and polyvinyl alcohol (PVA). Then magnetic separation technology could make the separation of solid and liquid phase easier. The combined technique of biosorption and magnetic separation holds the advantages of flexibility, eco-friendly characteristics, and economic in operational cost. Thus, the current investigation into this technique is very important and inspiring.

5.5 Comparative Conclusions of the Methods

Every before-mentioned method for heavy metal removal, especially biosorption has actually its advantages and disadvantages for recovering heavy metals. This means in some cases, two or more methods may be chose to treat the target solution to work their way through drastically. Please refer to Table 5.9 for detail.

5.6 Recovery and Reuse of Heavy Metal

Heavy metal ions from the contaminated water could be reduced into metal nanoparticles by physical, chemical, and biological technology [277, 278]. Most of these physical and chemical methods need extreme conditions like temperature, pressure etc. Chemical reducing agents are believed to be associated with environmental toxicity or biological hazards, whereas comparatively safer reluctant like citrate, ascerbate, simple sugars like glucose, fructose etc. are not efficient in productivity. It has been, therefore, of increasing interest to develop efficient green biological reduction [278]. What is more, current chemical methods of metal nanoparticle synthesis have shown limited success and is expected that the use of a biological approach may overcome many of these obstacles. The exploitation of microorganisms for the biosynthesis of metal nanoparticles is an area of research that has received increasing interest over the last decade. The use of living microbes as a tool for nanoparticle biosynthesis has been researched extensively [279]. The size and shape-dependent physicochemical and optoelectronic properties of metal nanoparticles have important applications in catalysis, biosensing, recording media, and optics and so on [280]. For example, gold nanoparticles (Au NPs) have potentially exciting applications in hyperthermia of tumors, optical coatings, and scanning tunneling microscopes as conductive tips [281]. Especially, biological method available for low metal concentration, less than 100 mg/L, could exert the advantage of simple course, easy operation, low cost, little pollution, and high recovery rate of heavy metal etc. [18]. If all of the removal technologies could be applied in to commercial production, not only effluents are purified but also the toxic heavy metal ions are effectively reused to make a green and perfect recycle between the nature and our industrial society. In sum, researches on heavy metal removal give a wide vision and a promising future to development of all the fields.

5.7 Current Hot Topics, Trends, and Outlook of This Field

Nowadays, more researche has been focused on the search for alternative and innovative wastewater treatment techniques. The interesting one was the utilization of biological materials such as algae, fungi, and bacteria for the metal removal and

Table 5.9 Advantages and disadvantages of the methods

Methods	Advantages	Disadvantages
Activated carbon	High surface area	High cost to prepare activated carbon Reactivation results in a loss of the carbon Performance dependent on the type of carbon used and non-selective
Chemical precipitation	Effectively treat inorganic effluent with a metal concentration of higher than 1,000 mg/L with a simple process	The demand of a large amount of chemicals Generally it cannot be used to handle low concentration of metal wastewater, which is below 100 mg/L The long-term environmental impacts of sludge disposal Used as a pretreatment for wastewater treatment Inadequate selectivity
Chemical redox	Be applicable for several metal ions	High energy consumption
Membrane separation	Can be application in occasions where the concentration of metal ions is low	Immature technologies Suitable ion exchange resins are not available for all heavy metals
Ion exchange	Effective to treat inorganic effluent with a wide metal concentration of less than 10 mg/L to higher than 100 mg/L Does not present any sludge disposal problems	The capital and operational cost is high Early saturation can be problem i.e. when metal interactive sites are occupied, metal desorption is necessary prior to further use, irrespective of the metal value
Biosorption	Growth-independent, non-living biomass is not subject to toxicity limitation of cells Biomass can be procured from the existing fermentation industries, which is essentially a waste after fermentation. The process is not governed by the physiological constraint of living microbial cells Because non-living biomass behave as an ion exchanger, the process is very rapid and takes place between few minutes to few hours. Metal loading on biomass is often very high, leading to very efficient metal uptake Because cells are non-living, processing conditions are not restricted to those conducive for the growth of cells. In other words, a wider range of operating conditions such as pH, temperature and metal concentration is possible. No aseptic conditions are required for this process Metal can be desorbed readily and then recovered if the value and amount of metal recovered are significant and if the biomass is plentiful, metal-loaded biomass can be incinerated, thereby eliminating further treatment	The potential for biological process improvement (e.g. through genetic engineering of cells) is limited because cells are not metabolizing. Because production of the adsorptive agent occurs during pre-growth, there is no biological control over characteristic of biosorbent. This will be particularly true if waste biomass from a fermentation unit is being utilized There is no potential for biologically altering the metal valency state. For example less soluble forms or even for degradation of organometallic complexes

recovery among these techniques [21]. In other studies, biomasses have exhibited economic, rapid adsorption, and eco-friendly characteristics [2]. However, it is still necessary to continue the steps towards the world of these promising biosorbents from an extremely large pool of readily available and inexpensive biomaterials [8, 9]. The mechanism involved in metal biosorption is far from well understood up to date. It is the mission of this field to investigate the microbe-metal interactions and obtain the mechanism of metal uptake by biosorbents and then grasp this tool to change the world.

Also in the field, it is a hot and rising topic to synthesize metallic nanoparticles using biological technology by simultaneously reducing heavy metal ions level in the wastewater. The development of these green techniques for the controlled synthesis of metallic nanoparticles of well-defined size and shape is a big challenge and numerous chemical methods, aimed at controlling the physical properties of the particles, are still in the development stage and problems are often experienced with stability of the nanoparticle preparations, control of the crystal growth, and aggregation of the particles [115, 117, 118]. Although, these researches are still in their infancy of theoretic and experimental phase, the coming fruits are sure to be of excitingly wide perspective and practicability in the near future.

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