Chapter 4
Biosorption of Heavy Metal from Aqueous Solutions

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4.1 Introduction

Massive quantities of metals from anthropogenic source are both accidental and considered released into the environment throughout the year as the population number and industrialization increased. Toxic metals in concerned include emissions of heavy metals from industries, mine tailings, leaded gasoline, paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, and atmospheric deposition can accumulate and persist in the ecosystem. Consequently, removing these substances from discharges before they enter the ecosystem has turned into a challenge for environmental engineering in our time. The conventional methods for treating metal-containing wastewaters are coagulation and flocculation, reverse osmosis, electrochemical, and activated carbon adsorption [1]. None of these technologies show both significant effectiveness and economic advantage in metal removal. However, activated carbon seems to be the most effective and widely used adsorbent but with a certain problem of its use. The higher prices of it correspond to higher levels of the quality. Furthermore, regeneration of activated carbon is almost impossible [2].

Biological materials, living or dead cell, have long been investigated in their capabilities to remove metal ions [1, 3]. Generally, there are such interactions between living things and metals, as the uptake and storage of essential and nonessential metals by the dead and living cells have been studied. Some organisms have developed mechanisms to uptake and store higher concentration of those metals and, hence, some species can also detoxify some toxic metals [4]. Both living and dead cell have a basic property to bind with not only inorganic but also organic chemicals and can concentrate the much diluted chemicals in solution [5, 6]. These

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involved the consideration for an economy approach for metal-contaminated water cleanup. Bioremediation methods to clean up toxic metals from water discharge take account of biosorption, the use of biological materials to accumulate those metals through many metabolic or biochemical pathways and then concentrated them from solution [7, 8]. The biological materials used in biosorption to remove target substances from solution or biosorbents are derived from various types of origins including bacteria, yeast, fungi, algae, plant, and animal products such as chitosan [9] and crab shell [10]. Based on the metal uptake capacity, biosorbents used in practical application should hold some characteristics that improve its performance in engineering perspectives. These are: cost of biomass, selectivity of metal-binding sites, and resistance to wide range of physical and chemical conditions. Conventional techniques of biosorbent production and kinetics of biosorption from different species of organisms will be discussed as well as the appropriate immobilization techniques.

4.2 Biosorption of Metal

There are two general basic terms of sorption, absorption, and adsorption. Absorption is a process which atom or molecule of one phase interpenetrates practically uniformly within those of another phase to form a solution with it [11]. In the other way, adsorption is often used to designated the accumulation of substances that can take place at a surface or interface of any two phases, liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface for example [11]. Accordingly, the absorption process does not count as a biosorption mechanism in this chapter. In addition, there are three major characteristics of adsorption. The first consists of electrical attraction or exchange adsorption which is the relation between microbial negatively charged ligands and positively charged ions. The second adsorption characteristic is physical or ideal adsorption which includes van der Waals force which the adsorbed molecule can have translational movement within the interface. The last one is chemical or activated adsorption which is chemical attraction between adsorbent and the adsorbate [12]. In general, it is difficult to separate physical and chemical characteristic from each other and these three usually collaborated in adsorption.

Biosorption, as defined by Naja and Volesky [11], is an operation that combines the use of biomaterials for sorbing, sequestering, and immobilizing both inorganic and organic compounds from aqueous solution. Biosorption is the capability of nonmetabolizing biomass to bind and concentrate selected ions or other molecules from aqueous solutions based on the passive sequestration, and this mechanism is opposed to a much more complex phenomenon, bioaccumulation which is based on active metabolic transport [13]. The passive uptake of metal by biosorption may arise by one or a combination of different processes including complexation, coordination, chelation, ion exchange, microprecipitation, and entrapment [14]. Most of

the passive uptake mechanisms are associated with either non-metabolizing or metabolizing cells with the exception of microprecipitation and entrapment which usually refer to immobilization of metal species in the solid form that located outside or inside the cells, such as the extracellular polymeric capsule or cytoplasmic compounds [11].

In immobilization or sequestration of metal, the use of non-metabolizing or nonliving cells offers some benefits over the metabolizing or living cells. In metabolizing cells, the active metabolic activities may influence biosorption by changing the environmental factors such as pH, Eh, and also the metabolites in cellular microenvironment. The other important reason of using the living cells in biosorption is practically that all biological macromolecule as well as cell walls and other associated biomolecules have some affinity for metal species. Additionally, there could be accurate control of the metal removal process using non-metabolizing biomass in specific removal system. For the purpose of removing dissolve metal from aqueous solution, metal immobilization or dissolve metal bonded to form a solid particle is easier to separate. The nonliving biomass deposited with metal ions can be removed together by solid–liquid suspension system including settling, flotation, centrifugation, and filtration.

4.2.1 Biosorbent

For economic reasons in metal biosorption, of particular interest are abundant biomass types either generated as a waste by-product of large-scale industrial fermentations or certain metal-binding algae found in large quantities in the sea or even microorganisms are fascinating within the past decades [15]. At least four broad areas of application for biosorbent materials have been considered which include detoxification of metal-bearing wastewaters, decontamination of radioactive wastewaters, recovery of metals from ore processing solutions, concentration or recovery of rare metals from seawater [16]. Biosorbents proposed for application need to be derived usually as granules of classified size ranges between 0.1 and 3 mm with a preferred rigidity to resist pressure in the column and water permeability. They may be chemically pretreated for better performance and/or suitability for process applications.

Biosorbents are biological materials capable of directly sorbing metal ionic species from aqueous solutions [11]. The key challenge for the biosorption was to select the most favorable types of biomass from available and inexpensive biomaterials [17]. Although many biological materials can bind metals, only those with appropriately high metal-binding capacity and selectivity for metals are suitable for a full-scale biosorption process. The biosorbent materials among easily available include three groups: bacteria, algae, and fungi, the latter two possibly giving broader choices [18].

4.2.2 Bacterial Biosorption

Bacteria are a main group of unicellular organisms belonging to the prokaryotes, which are abundant in environment especially in soil and water. They have simple morphology and present in three basic shapes: spherical or coccus, rod or bacillus, and spiral or spirillum. Bacteria vary both in size and shape. The typical size of bacteria cell is about 1.1–1.5 μm wide by 2.0–6.0 μm long. Cell size is an important characteristic for an organism as it affects a number of cell biological properties. Small size of bacteria ensures rapid metabolic processes.

The cell wall is the important for structure for bacterial cell and its main function including providing cell shape and protecting it from osmotic lysis; protecting cell from toxic substances; offers the site of action for several antibiotics; and the last one is the necessity for normal cell division. Bacterial classification by Gram staining technique, the Gram-positive bacteria stained purple, whereas Gram-negative were colored pink or red. The surface of Gram-negative cells is much more complex chemically and structurally than that of the other but the walls of Gram-positive cells are stronger because of the thicker peptidoglycan layer [18].

Gram negative bacterial cell wall has a 2–7 nm peptidoglycan layer surrounded by a 7–8 nm thick outer membrane. The peptidoglycan is covalently bound to the outer membrane by lipoproteins and sandwiched between the plasma membrane and the outer membrane, which is composed of phospholipids, lipopolysaccharides (LPSs), enzymes, and other proteins, including lipoproteins. The Gram-negative bacteria also have various types of complex macromolecular lipopolysaccharide and each LPS is held in the outer membrane by relatively weak cohesive forces, ionic and hydrophobic interactions and can be dissociated from the cell surface with surface-active agents. The net negative charge of LPSs attributes to the negative surface charge of Gram-negative bacteria. The phosphate groups within LPSs and phospholipids have been proved to be the primary sites for metal interaction. However, only one of the carboxyl groups in LPSs is free to interact with metals [19].

Using bacteria as biosorbent are promising because of their small size, ubiquity, and the ability to grow under controlled conditions. Additionally, they have capability to survive in a wide range of environmental situations. Bacteria may either retain the capacity for biosorption of many elements depending on the species, in some cases, may be element specific [18]. Many biosorption of metal are established such as cadmium biosorption by *Sphingomonas paucimobilis* biomass [20] *Arthrobacter* sp. [21], *Bacillus* sp. [22], and other [23]. Bacterial exopolysaccharide (EPS) consisting of extracellular DNA, lipids, polysaccharides, and proteins also studied their metal ion biosorption properties [24]. Immobilization of biosorbent seemed to work very efficiently. Rangsayatorn et al. [25] found that cadmium biosorption by immobilized cyanobacteria, *Spirulina platensis* TISTR 8217 on alginated gel and silica gel show the maximum capacities at 70.92 and 36.63 mg Cd/g biomass, respectively, and the immobilized cell could be repeatedly used up to five times (Fig. 4.1 and Table 4.1).

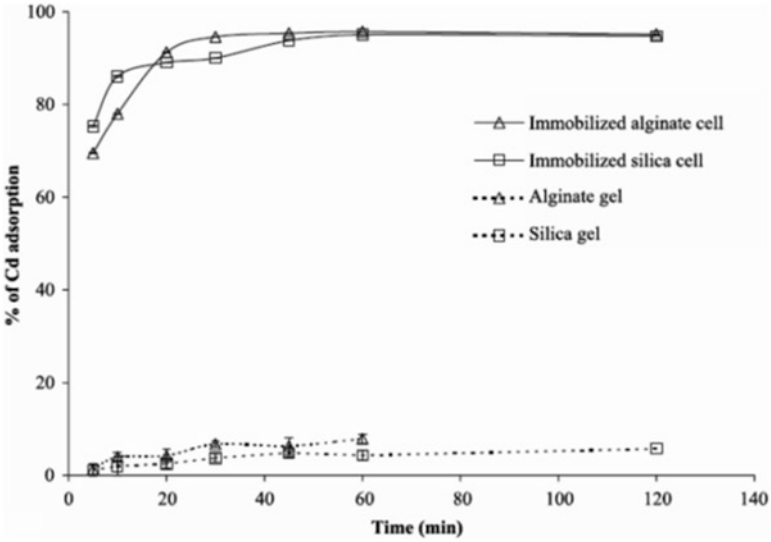

Fig. 4.1 Time course of cadmium removal by *S. platensis* immobilized on silica gel and alginate gel. Reproduced from Rangsayatorn N., Pokethitiyook P., Upatham E.S., Lanza G.R. 2004. Cadmium biosorption by cells of *Spirulina platensis* TISTR 8217 immobilized in alginate and silica gel. Environ. Inter. 30:57–63 [25], with permission of Elsevier

Table 4.1 Five cycles of cadmium adsorption–desorption using 0.1 M HCl as a desorbing agent

	% of cadmium adsorption[a]	
Cycle	Alginate-immobilized cell	Silica-immobilized cell
1	94.07 ± 0.06	92.67 ± 0.02
2	70.79 ± 0.15	66.99 ± 0.27
3	65.85 ± 0.34	78.31 ± 0.24
4	65.85 ± 0.11	78.47 ± 0.14
5	66.73 ± 0.71	63.21 ± 0.16

Reproduced from Rangsayatorn N., Pokethitiyook P., Upatham E.S., Lanza G.R. 2004. Cadmium biosorption by cells of *Spirulina platensis* TISTR 8217 immobilized in alginate and silica gel. Environ. Inter. 30:57–63 [25], with permission of Elsevier

[a]The values given are means ± SD

4.2.3 Fungal and Yeast Biosorption

Fungi can be clustered into molds or yeasts based on thallus development and most of them are filamentous. Yeasts are unicellular fungi that reproduce either asexually by budding and transverse division or sexually through spore formation. A mold such as *Penicillium* and *Aspergillus*, consists of long, branched, thread-like filaments of cells, hyphae, which form a tangled mass called a mycelium. The fungal

hyphae are typically 5–10 μm wide but may vary depending on the species and a common cytoplasm exists throughout the hyphae. The hyphae walls are composed of cellulose or chitin or both of them.

In general, yeast colonies are much like those of bacteria but yeast cells are larger than bacteria with the size about 2.5–10 μm wide by 4.5–21 μm long. Yeast cell is commonly spherical to oval shaped depending on species, nutrition level, and also culture condition. The most important commercial yeasts are member of the genus Saccharomyces, the baker's and brewer's yeasts which are eukaryotic cells. They are excellent models for eukaryotic biology study especially for *S. cerevisiae*. Generally, yeast cells have a cell wall and most of the other eukaryotic organelles but lack of flagella.

The cell walls of the fungi are inflexible and provide structural support and shape, but they are different in chemical composition from prokaryotic cell walls with mainly 80–90 % polysaccharide, with proteins, lipids, polyphosphates, and inorganic ions. Chitin is a common constituent of fungal cell walls. Fungal cell wall consists of two layers, a thin outer layer consisting of mixed glycans, and a thick inner layer of microfibrillar polysaccharide fibers composed of chitin or cellulose. The cell membrane of eukaryotic cells is a thin, double-layered sheet composed of lipids, such as phospholipids and sterols and protein molecules. Cytoplasmic membranes served as selectively permeable barriers in transport. In contrast with prokaryotes, eukaryotic cells contain a number of individual membrane bound organelles that are extensive enough to account for 60–80 % in volume [18].

The metal ions are compartmentalized into different subcellular organelles, e.g., mitochondria and vacuole, after entering into the cell thus cytoplasm is important for living cells to interact with metal ions [26]. Limiting metal uptake by active excretion, storage in an inert form or stored metal excretion are the main approaches for essential metals. In contrast, excretion from the metal excess pool and internal storage without elimination are the major approaches for nonessential metals and the metal concentration in the cells will increase with elevating external concentration. Vijver et al. [26] pointed out that the cellular sequestration mechanisms mainly have two types, the formation of distinct inclusion bodies and the binding of metals to heat-stable proteins. The former the formation of distinct inclusion bodies includes three types of granules: (a) amorphous deposits of calcium phosphates, e.g., Zn, (b) mainly containing acid phosphatase, accumulating, e.g., Cd, Cu, Hg, and Ag; and (C) excess iron stored in granules as hemosiderin. The latter mechanism mainly relates to a specific metal-binding protein, metallothioneins (MT), which can be induced by many substances, including heavy metal ions, such as Cd, Cu, and Hg. The used of fungal group also extensively examined such as unmodified yeast cells of *S. cerevisiae* to remove Pb(II) and Cu(II) ions from aqueous solutions in continuous mode was studied [27] and Cu biosorption onto fungal *Rhizopus oligosporus* [28].

4.2.4 Algae and Plant Material Biosorption

Algal diversity can be defined based on phylogenetic relationships, life stage, morphological types, habitats occupied by different groups, or their chemical diversity. Their habitats range from open oceans which occupied by microalgal planktonic species to rocky shores which may be marine macroalgae or seaweeds, and benthic microalgae. Some algae occupy freshwater habitats including rivers, lakes, ditches, and ponds which are the group of conspicuous filamentous algae. Not as much observable are the benthic microalgae which populate bedrocks in various damp and temporarily damp marine, freshwater, and terrestrial habitats. The diversity of algal taxonomy with different habitats put forward that different species have evolved equivalent metabolic pathways, though not necessarily through a shared evolutionary pathway, to fulfill basic processes such as protection from biotic and abiotic stresses [29].

Microalgae are unicellular or colonial algae and can exist in filamentous form. Most of them contain chlorophyll but a few kinds of common algae are not green but appear brown or red because other pigments such as carotenoids are present in addition to chlorophyll. Algae cells contain one or more chloroplasts, membranous structures that house the photosynthetic pigments [18]. Algae demonstrate significant diversity in their cell wall structure and chemistry. In several cases, the cell wall is composed of a network of cellulose fibrils and usually modified by other polysaccharides adding such as pectin, alginic acids, or fucinic acid. In some algae, the wall is calcium carbonate deposition, where occasionally chitin is also present. Cell wall is absent in euglenoids whereas silica, protein and polysaccharide are added in cell wall of diatoms. Similar to the fungal cell wall in structure, the algal cell wall is made of multilayered microfibrillar framework containing cellulose which presented mostly about 90 % of the algal cell wall and interspersed with amorphous material consisting of glycoproteins.

In biosorption, various algae or seaweed were used and investigated as biosorbents for metal removal due to their high sorption capacity and their ready availability in practically unlimited quantities in the seas and oceans such as Brown Seaweed, Lobophora variegate [30, 31]. There are also a number of plant biosorption studies including fern biomass [32], duckweed [2], and many aquatic macrophytes such as batch and continuous packed column studies of cadmium biosorption by *Hydrilla verticillata* biomass [33] and other work [34].

4.2.5 Additional Biosorbent Extensively Used in Biosorption of Heavy Metals

Various kinds of adsorbents have been widely produced an applied for the removal of radionuclides and heavy metals such as chitin, a natural long chain polysaccharide polymer of *N*-acetyl-D-glucosamine. It is the main component of the

exoskeletons of arthropods such as crustaceans. It is acid resistance and recognized as an excellent metal ligand, forming stable complexes with many metal ions [35]. Chitin can use as biosorbent in many forms such as acid wash crab shell [10], shrimp shell flakes [35], chitosan nanoparticles, and crab shell particles [9]. The alternative biomaterials that have high efficiency to remove metal ion from solution along with bark [36] and saw dust which produced in large quantities at sawmills as a solid waste and also contains primarily lignin and cellulose [37, 38] as well as many unusual biosorbent were examined including pollen pini [39] and human black hair as source of melanin granule [40].

4.3 Factors Affecting Metal Biosorption

Biosorption is affected by an amount diverse of physicochemical mechanisms, depending on many external environmental factors as well as on speciation of elements in solution.

4.3.1 pH

One of the most important environmental factors on metal ions biosorption is pH. It strongly impacts not only the binding site of the biomass, but also the chemistry of the metals including hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation, speciation, and biosorption availability of the heavy metals [41]. Meanwhile ion exchange is the major mechanism-driven biosorption and protons compete with metal cations for the binding sites, pH is the key condition which powerfully affects the process [7]. The different metal species occurring at different pH values also have variable charges and adsorption ability at solid–liquid interfaces. The pH not only limits solubility of toxic metal ions but also affects the properties of biomass. Many metals are free hydrate species at acidic condition and after pH increases, hydroxides are formed and precipitation of metal may be occurring. In addition, pH effects negative charge level on biomass surface by either protonation or deprotonation of metal-binding sites.

As pH increase, metal ions in solution are likely to undergo hydrolysis, but their degree will be differing at different pH values with each metals. The typical series of hydrolysis involves the formation of hydroxylated monomeric species followed by the formation of polymeric species and then crystalline oxide precipitation after aged [42]. The different pH sorption capability for metal ions may possibly relate to the nature of chemical interaction of each metal with biomass. The uptake of heavy metal cation by most biomass types decreases as the pH decreases as most of the heavy metals precipitate at pH higher than 5.5 [25]. It is supposed that metals might accumulate inside the cell or cell wall at more alkaline condition by a combined sorption-microprecipitation mechanism [17].

The optimum pH for metal biosorption differs for each ion and both cations and anions express different sorption pattern on the same biomass in the same pH range. Principally, the negative charge of cell surface increase as pH increase until all significant functional groups are deprotonated, which favors electrochemical attraction and cation adsorption and cations may have more capability to compete for binding on cell surface with H+. In contrast, anions have a tendency to intensely interact with binding sites as their positive charge concentration increase due to the protonation of functional groups at acidic conditions [7]. Biomass can be noticed as natural ion-exchange materials that contain weakly acidic and basic groups which follow the theory of acid–base equilibria that, in the pH range 2.5–5, the binding of heavy metal cations is determined by the state of dissociation of the weakly acidic groups. Solution pH as well affects the surface properties of biomass because the adsorption capacity of biomass is as a result of anionic or polar chemical group on their surface [43].

There are diverse natural groups of chemical on biomass surface which influence the adsorption capacity including carboxyl, phosphate, amine, amino, hydroxyl, and sulfhydryl. The pH dependence of metal uptake pointed to the weak acidic carboxyl groups R–COOH of algal and fungal cell wall components and also R–COOH groups of peptidoglycan in Gram-positive bacteria as the probable sites of ion exchange (Fig. 4.2). Carboxyl groups in biological polymers have pK_a values ranging from 3.5 to 5.0 [44]. The metal binding to the carboxyl group increased with the pH up to 4.1, but slightly decreased over the optimum pH, because of competitive binding sites. With increasing pH, the carboxyl group free sites increased because most of the metal is present in the biomass phase, and only a low level is present in the solution.

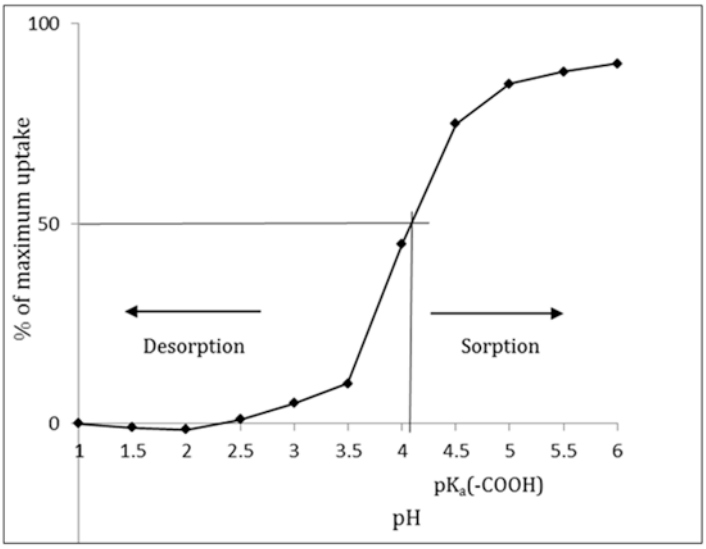

Fig. 4.2 Metal biosorption equilibrium as a function of pH in algal and fungal cell wall. Carboxyl groups (R–COOH, pK_a in the range of 3.5–5.5) of algal and fungal cell wall constituents as the probable sites of ion exchange. Reproduced from Kratochvil D., Volesky B. 1998. Advances in the biosorption of heavy metals. Trends. Biotechnol. 16:291–300 [17], with permission of Elsevier

The other such as phosphonate groups of plasma membrane phospholipids in brown seaweed have a similar range of the pK_a value whereas the amine group with pK_a values in various biomaterials ranging between 8 and 10. The positively charge, amide in crab shell chitin and chitosan, offered their binding sites for negative metal ion, increase as pH of aqueous solution decrease especially for anionic arsenate, $H_2AsO_4^-$ [10]. Uranium biosorption by shrimp flakes [35] increased with an increase in pH of the solution and when pH was over 3.6 the q_e values decreased. This could be explained that at slight acidic solution, amine groups in the flakes easily form protonation that induced an electrostatic repulsion of metal ions. Arsenate biosorption is not only determined by the acid–base properties of functional groups on the biomass but also by its chemical speciation in the solution which tends to hydrolyze depending on the solution pH.

4.3.2 Temperature

Dissimilarly with temperature independent non-metabolizing cells, the metabolizing cells are temperature dependent and the alteration of this factor will strongly affect the biosorption process. Naturally, adsorption and ion exchange are exothermic and therefore their reaction rate increase when temperature increases. On the other hand, the biosorption possibly will decrease at very high temperature due to cell walls damaged. Most of metal uptake increased when temperature increased in the range of 4–13 °C, while only a marginal decreased when temperature increased from 20 to 40 °C (Table 4.2) [7, 25].

If adsorption increases as temperature increases, it may be indicative of chemisorption; whereas decrease in adsorption with increasing temperature may be because of physical adsorption [36]. However, the biosorption evaluation at room temperature is still appropriate because it is fit to be replicated as demonstrated in uranium adsorption by shrimp shell flakes that the uranium adsorption efficiency decreases with the increase in the temperature and the highest adsorption efficiency occurs at room temperature after that the adsorption efficiency decreases to reach the lowest values at 70 °C [35].

Table 4.2 Effect of temperature on cadmium adsorption by immobilized *S. platensis*

	% of cadmium adsorption[a]	
Temperature (°C)	Alginate-immobilized cell	Silica-immobilized cell
20	96.20 ± 0.11	95.48 ± 0.06
26	92.32 ± 0.01	94.72 ± 0.02
30	94.72 ± 0.04	92.96 ± 0.09
40	94.88 ± 0.07	92.68 ± 0.10

Reproduced from Rangsayatorn N., Pokethitiyook P., Upatham E.S., Lanza G.R. 2004. Cadmium biosorption by cells of *Spirulina platensis* TISTR 8217 immobilized in alginate and silica gel. Environ. Inter. 30:57–63 [25], with permission of Elsevier

[a]The values given are means ± SD

4.3.3 Initial Metal Ion Concentration

Initial higher concentrations of metal ions have some effects on biosorption which resulting in a high metal uptake. The reason is at lower metal concentrations the ratio of ion to the available surface area declines; afterward the fractional sorption becomes independent of metal initial concentration. Conversely, at high metal concentrations, the availability of sorption sites decrease comparing to the ion numbers and then the metal removal is strongly rely on initial metal concentration [7, 41]. This occurrence also discovered in Srivastava et al. [36] which gradual decrease in percentage removal of Cr (VI) by native and chemically modified *Lagerstroemia speciosa* bark with an increase in initial ion concentration. This incidence occurred because of limited number of active sites on the biosorbent, which would have become saturated above a certain concentration. Increase of the initial Cr(VI) concentration results in a decrease in the initial rate of external diffusion and increase in the intraparticle diffusion rate.

4.3.4 Initial Biosorbent Concentration

The levels of metal biosorption strongly govern by biosorbent quantity. As biomass increases, metal biosorption also increases as a result of the biomass surface area increase, which in turn raises the binding sites number [7, 42]. In contrast, increasing biosorbent concentration decreases the quantity of metal sorption per unit of biomass weight due to the complex factors. The significant factor affecting biosorption at large amount of biosorbent is the deficiency of available metal to completely cover the available exchangeable sites resulting in low metal uptake. The interference between binding sites due to increasing biomass number cannot be taken precedence because low specific uptake may occur [7]. Ahmed et al. [35] reported that the adsorption efficiency increased with the initial metal concentration varying from 50 to 875 mg/L. They suggested that with more uranium content in a solution, larger fraction of the active sites is involved in the adsorption process then the increase in adsorption efficiency becomes less significant at 175.8 mg uranium/L, where 85 % from uranium was grafted on 1 g shrimp shell flake sand.

4.3.5 Effect of Contact Time

A passive physical adsorption of metal at the cell surface is very fast and takes place in a very short time after metal ions contact with the biosorbent. This behavior suggests that in the initial stage adsorption takes place rapidly on the external surface of the biosorbent followed by a slower internal diffusion process, which may be the rate limiting step. This is important because equilibrium time is one of the

parameters for cost-effective wastewater treatment plant application [41]. The biosorption of Eu(III) using chitosan nanoparticle and crab shell particle significantly rapidly increased from within 15 min after metal ion contact with those two biosorbent, thereafter reached saturation in 1 h. After the equilibrium period, the amount of metal adsorbed did not change further with time [9, 33].

4.3.6 Speciation of Metal Ions

Metal ion in biosorption process can be separated into two phases, a solid and liquid. Metal first dissolved in the solution then sequestered on biosorbent, the solid phase, accordingly the properties and behavior of both metal ion and biosorbent in solution influence the biosorption performance. After dissolving, most of the common metals perform in the solution as positively charged cations including more toxic heavy metal group, Pb, Hg, Cd, Cu, Zn, Ni, U, and Th, for example [11]. More common negatively charged anionic metal species such as As, Se, V, and Mn are occurring in more complex forms. These differences in metal speciation are specific to positively and negatively charge of biosorbent biding sites and thus affect the biosorption process.

4.3.7 Presence of Co-ions

Wastewater commonly contain a number of metal species and this phenomenon is expected to cause cooperative effects as a function of many factors including co-ion competing for biding sites, metal concentration and biosorbent quantity. Lower metal uptake from mixed solution commonly observed comparing to those in a single species. In general, metal uptake increases as the ionic radius of metal cation increases, with metals having higher ionic charge presenting larger binding to biomass. Additionally, the reduction level of metal uptake in the presence of other cations is found to be dependent on concentration of the other cations, indicated that as the concentration of other cations increases, the metal uptake decreases.

To observe the ionic competition effects in solution during the biosorption, the concept of Pearson's classification of the elements is used [45]. According to the Pearson's, based on the chemical coordination characteristics of the elements, the elements are classified into three main groups: class A or hard ions, class B or soft ions, and class C or borderline ions. Class A elements tend to form ligands preferably with oxygen as a donor atom where B elements tend to coordinate better with ligands of decreasing electronegativity. The last group, borderline elements are characterized by intermediate coordination behavior. Each class of elements may possibly exhibit for different biosorbent-binding sites, depending on their structural chemistry [46]. The study by Bunluesin et al. [33] has found that the presence of Zn had an antagonistic effect on Cd biosorption (Fig. 4.3). The breakthrough point of the Cd-Zn mixed solution was 3900 mL, whereas, that of the Cd solution alone was

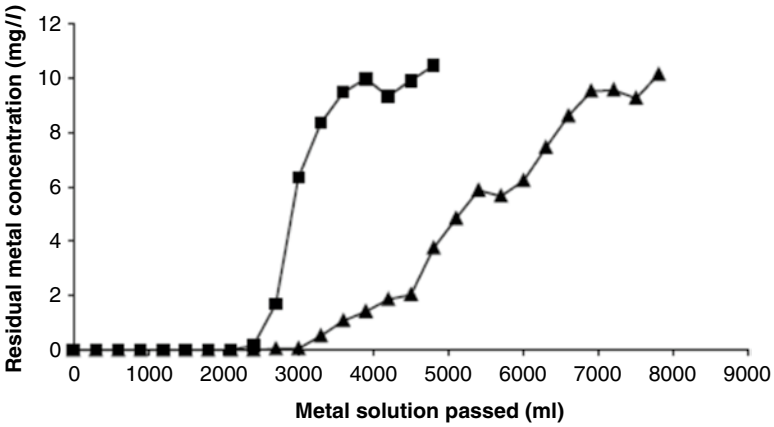

Fig. 4.3 Biosorption of Cd in mixed Cd and Zn solution in fixed bed column with continuous flow. Conditions: initial Cd and Zn concentration, 10 mg/L; pH5; actual flow rate 12.96 mL/min; 1 g of dry biomass; 25 ± 2 °C. Symbols: triangles, Cd; squares, Cd + Zn

at 7800 mL. This finding has shed some lights on the competition of different cations for biosorbent-binding sites.

4.4 Biosorption Isotherm and Kinetic Model

Biosorption can be defined as a cooperative term for several passive accumulation process including ion exchange, coordination, complexation, chelation, adsorption, and microprecipitation. At equilibrium, concentrations are a function of temperature, for that reason the adsorption equilibrium correlation at a specified temperature is mentioned as an adsorption isotherm [7, 47]. The solid–liquid sorption system assessment is typically based on two types of examinations: equilibrium batch sorption tests and dynamic continuous-flow sorption studies. Equilibrium isotherm model equations such as Langmuir and Freundlich are used in batch mode to describe experimental data, and it is important to find the best-fit isotherm to evaluate the efficacy of the prepared adsorbent to develop suitable industrial adsorption system designs [7, 13]. The Brunauer–Emmett–Teller (BET) model describes the multilayer adsorption at the biosorbent surface and assumes that the Langmuir isotherm applies to each layer [13].

4.4.1 Batch Biosorption Models

A typical biosorption batch design requires assessing the biosorbent quantity to process a given volume of a metal-containing solution. If sufficient time is allowed for equilibrium to be reached, the design of single stage batch systems is based on mass balances and thermodynamic equilibrium relationships.

The mass balance is given by:

$$V\left(c_o - c_e\right) = V_m\left(q_e - q_o\right)$$

where c_o and c_e are the initial and final metal concentration in the bulk solution, q_o and q_e are the initial and final metal concentration in the biosorbent, V is the volume of solution, and V_m is the volume of biosorbent. q_o is of course equal to zero when a biosorbent initially free from the metal contaminant is used. However, unlike gas-phase isotherms that generally function by temperature, liquid-phase isotherms are strongly affected by solution pH and ionic strength. In general, the equilibrium isotherm for a given metal–biosorbent system may not be expected from theory [48].

4.4.2 Equilibrium Isotherm

4.4.2.1 Freundlich Isotherm

Freundlich isotherm is an empirical equation that widely used for the adsorption equilibrium explanation. This isotherm can use for describing the heavy metals adsorption on diverse biosorbent types. This equation has the following form:

$$q_e = K_F C_e^{1/n}$$

It can also be expressed in the linearized logarithmic form:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

The plot of log q_e versus log C_e has a slope with the value of $1/n$ and an intercept magnitude of log K_F. Log K_F is equivalent to log q_e when C_e equals unity. However, in case when $1/n \neq 1$, the K_F value depends on the units upon which q_e and C_e are expressed. On average, a favorable adsorption tends to have Freundlich constant n between 1 and 10. Larger value of n or smaller value of $1/n$ implies stronger interaction between biosorbent and metal, whereas $1/n$ equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites [13, 47].

4.4.2.2 Langmuir Isotherm

Langmuir equation is a well-known used model that relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. This isotherm use for describing heavy metal sorption onto biosorbent based on three assumptions, adsorption is limited to monolayer coverage, all surface sites are the same and only can provide accommodation to one adsorbed

atom, and the ability of a molecule to be adsorbed on a given site is independent of its neighboring sites occupancy [47]. By applying these assumptions and a kinetic principle, in case that rate of adsorption and desorption from the surface is equal, the Langmuir equation can be written in the following form:

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e}$$

where q_e is the amount adsorbed, C_e the equilibrium concentration, $q_{\max}$ the saturated monolayer adsorption capacity, and K_L the sorption equilibrium constant.

The linear form of this equation is often written as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{K_L q_{\max}}$$

Within the Langmuir model, the saturation capacity $q_{\max}$ is supposed to correspond with saturation of a fixed number of identical surface sites, and it should reasonably be independent of temperature [8, 13, 47]. The decrease of K_L value with an increase in temperature indicates the exothermicity of the adsorption process or physical adsorption, while the opposite trend illustrates that the process needs thermal energy or endothermic which leads to chemical sorption. At higher temperature, the physical adsorption between metal and biosorbent active sites weakens; on the other hand, chemisorption becomes stronger. The exothermicity and endodermicity of biosorption can be determined by means of the heat of adsorption and commonly obtained through an integrated Van't Hoff equation, which relates the Langmuir constant, K_L, to the temperature:

$$K_L = K_o \exp\left(-\frac{E_a}{RT}\right)$$

where K_o is the adsorption equilibrium constant, E_a the activation energy of adsorption/heat of adsorption, R the gas constant (0.0083 kJ/(mol K)), and T the absolute temperature (K) [7].

4.4.2.3 Temkin Isotherm

The Temkin isotherm is based on the assumption that the decline of heat of sorption as a function of temperature is linear rather than logarithmic, as implied in the Freundlich equation [30, 49]. The Temkin isotherm has the form:

$$q_e = \frac{RT}{b} \ln\left(aC_e\right)$$

where b is the Temkin constant in relation to heat of sorption (kJ/mol) and a as the Temkin isotherm constant (L/g).

Temkin isotherms are not capable of predicting biosorption equilibria. The complex phenomenon involved in liquid-phase adsorption is not taken explanation by this equation as the basis of the Temkin equation involves simple assumptions. As a result, this equation is often not suitable for the representation of experimental data in complex systems [7].

4.4.2.4 Brunauer–Emmer–Teller (BET) Model

The BET model is removing the restriction in the Langmuir model which assumed that adsorption only occurs on the unoccupied adsorption sites. Assuming that the initial adsorbed layer can act as a substrate for additional adsorption, and then the isotherm, instead of leveling off to some saturated value at high concentrations, is able to increase indefinitely. The same kinetics concept proposed by Langmuir is applied to this multiple layering process, i.e., the rate of adsorption on any layer is equal to the rate of desorption from that layer [7]. The simplified form of BET equation can be written in the following form:

$$q_e = q_{\max} \frac{BC_e}{\left(C_e - C_s^*\right)[1+\left(B-1\right)\left(C_e / C_s^*\right)}$$

where B is a constant related to the energy of adsorption and C_s^* the saturation concentration of solute (mg/L).

Remarkably, other ideal assumptions within this model, that is all sites are energetically identical along with no horizontal interaction between adsorbed molecules, may be correct for heterogeneous material and simple nonpolar gases but not for complex systems involving heterogeneous adsorbent such as biosorbents and metals. For that reason, this equation is unpopular in the interpretation of liquid-phase adsorption data for complex solids [47].

4.4.2.5 Redlich–Paterson Isotherm

Redlich–Paterson is another empirical equation, designated as the "three parameter equation," which is capable of representing adsorption equilibria over a wide concentration range [7]. This equation has the following form:

$$q_e = \frac{K_{\mathrm{RP}} C_e}{1 + a_{\mathrm{RP}} C_e^{\beta}}$$

where a_{RP}, K_{RP}, and β are Redlich–Paterson's parameters.

This equation reduces to a linear isotherm at low surface coverage and to the Langmuir isotherm when b is equal to 1. Redlich and Paterson incorporated the characteristics of Langmuir and Freundlich isotherms into a single equation. Two limiting behaviors exist, i.e., the Langmuir form for $b=1$ and Henry's law form for $b=0$ [47].

4.4.3 Kinetic Studies in Biosorption of Heavy Metals

Adsorption equilibria studies are important to conclude the efficiency of adsorption. Despite of this, it is also necessary to identify the adsorption mechanism type in a given system. Kinetic models have been exploited to test the experimental data to examining the mechanism of biosorption and its potential rate-controlling steps that include mass transport and chemical reaction processes. Information on the kinetics of metal uptake is required to select the optimum condition for full-scale batch metal removal processes as well [7].

Several adsorption kinetic models have been established to understand the adsorption kinetics and rate-limiting step which include pseudo-first- and pseudo-second order rate models, Weber and Morris sorption kinetic model, Adam–Bohart–Thomas relation, first-order reversible reaction model, external mass transfer model, first-order equation of Bhattacharya and Venkobachar, Elovich's model, and Ritchie's equation. The pseudo-first- and pseudo-second-order kinetic models are the most well-liked models to study the biosorption kinetics of heavy metals and quantify the extent of uptake in biosorption kinetics.

4.4.3.1 The Pseudo-First-Order Kinetic

The Lagergren first-order rate expression based on solid capacity is generally expressed as follows:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_1\left(q_e - q\right)$$

where q is the amount adsorbed at time t and k_1 the rate constant of first-order adsorption.

Integration of the above equation with the boundary conditions, $t=0$, $q=0$, and $t=t$, $q=q$, gives:

$$\ln\left(q_e - q\right) = \ln q_e - k_1 t$$

Theoretically, to determine the rate constants and equilibrium metal uptake, the straight-line plots of $\log(q_e - q)$ against t of above equation were made at different initial metal concentrations. The q_e value developed by this method is then

compared with the experimental value. If large discrepancies are posed, the reaction cannot be classified as first-order although this plot has a high correlation coefficient from the fitting process.

This equation can be written in the nonlinear form:

$$q = q_e\left(1 - \exp\left(-k_1 t\right)\right)$$

Nonlinear fitting of this equation is another way to achieve the predicted value of q_e and k_1 although this is not a common application. The trend shows that the predicted q_e values seem to be lower than the experimental values. A time lag, probably caused by the presence of a boundary layer or external resistance controlling the beginning of the sorption process, was discussed to be the responsible factor behind the discrepancy [7, 13, 50].

4.4.3.2 The Pseudo-Second-Order Kinetic

Expecting the adsorption rate for a given system is among the most important factors in adsorption system design, as the system's kinetics determines adsorbate residence time and the reactor dimensions [7, 13, 51]. Although various factors play important rule on the adsorption capacity including initial heavy metals concentration, temperature, pH of solution, biosorbent size, and heavy metals nature, a kinetic model is only concerned with the effect of recognizable parameters on the overall rate.

Pseudo-second-order model is derived on the basis of the sorption capacity of the solid phase, expressed as:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_2\left(q_e - q\right)^2$$

where k_2 is the rate constant for pseudo-second-order model. Integration of above equation with the boundary conditions $t=0$, $q=0$, and at $t=t$, $q=q$, results in:

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t$$

This equation can be stated in the linear form as:

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$$

The pseudo-second-order rate constants can be determined experimentally by plotting t/q against t, this model is considered more appropriate to represent the kinetic data in biosorption systems, in comparison to pseudo-first-order kinetic

intrinsically. Additionally, the pseudo-second-order model above has the highest coefficient of determination for the linear method. In contrast to the linear model, the subsequent kinetic parameters from the nonlinear model were almost identical among each other, as a result, the nonlinear method is considered as a better way to establish the preferred parameters [7, 13, 52]. Pseudo-first- and pseudo-second-order rate expressions have been and still in extensive use for the biosorption of heavy metals from aqueous solutions. In chemisorption process, the pseudo-second-order is superior to pseudo-first-order model as it takes into account the interaction of adsorbent–adsorbate through their valence forces [13, 51].

4.4.3.3 The Weber and Morris Sorption Kinetic Model

The Weber and Morris (WM) sorption kinetic model was initially employed by Pavasant et al. [53] to describe their biosorption experimental data. This model has the following form:

$$q = K_{\mathrm{WM}}\sqrt{t}$$

where K_{WM} is the Weber and Morris intra-particle diffusion rate. In their study, the Cu(II), Cd(II), Pb(II), and Zn(II) sorption process by *C. lentillifera* biomass was regulated by two main mechanisms, intra-particle diffusion and external mass transfer. The intra-particle diffusion (D) can be estimated with:

$$D = \frac{\pi}{8640}\left(\frac{\left(d_p K_{\mathrm{WM}}\right)}{q_e}\right)^2$$

where d_p is the mean particle diameter.

The external mass transfer process was determined by

$$\frac{\mathrm{d}q}{\mathrm{d}t} = K_L^{'} A\left(C - C_s^i\right)$$

where $K_L^{'}$ is the liquid–solid mass transfer coefficient, A the specific surface area of biomass, C the liquid-phase concentration of sorbate in the bulk solution at t, and C_s^i the concentration of sorbate in the inner pore of sorbent. They observed that the external mass transfer coefficients can be ordered from high to low values as Cu(II)>Pb(II)>Zn(II)>Cd(II), while the intra-particle diffusion coefficients were as follows: Cd(II)>Zn(II)>Cu(II)>Pb(II) [13, 53]. All biosorbents, equilibrium isotherms, and kinetic modeling performed by several researchers have been summarized in Table 4.3.

Table 4.3 Summary of the biosorbents, equilibrium isotherms, and kinetic modeling performed by several researchers

Metal	Biosorbent	Equilibrium isotherm	Kinetic modeling	Reference
U	Shrimp shell flakes	Langmuir model (25.31 mg/g)	Pseudo-second order (8.196 mg/g)	Ahmed et al. [35]
	Human black hair	Langmuir model (62.5 mg/g)	Pseudo-second order (2.99 mg/g)	Saini and Melo [40]
	Pollen pini	Freundlich isotherm (281 L/kg at pH2.5 and 2336 L/kg at pH5)	Pseudo-second order (16.06 g/kg at pH2.5 and 67.23 g/kg at pH5)	Wang et al. [39]
	An aquatic macrophyte, *Eichhornia crassipes*	Langmuir model (142.85 mg/g)	Pseudo-second order	Yi et al. [34]
Eu	Chitosan nanoparticle	Langmuir model (3.23 mg/g)	Pseudo-second order (0.0408 mg/g)	Cadogan et al. [9]
	Crab shell particle	Langmuir model (114.9 mg/g)	Pseudo-second order (0.3963 mg/g)	
Cr (VI)	Natural plant bark	Freundlich isotherm (9.272 mg/g)	Pseudo-second order (10.4167 mg/g)	Srivastava et al. [36]
	Chemically modified plant bark	Temkin isotherm (1.3128 L/g)	Pseudo-second order (0.8039 mg/g)	
	Sal sawdust	Langmuir model (3.6 mg/g)	Pseudo-second order	Baral et al. [38]
Pb (II)	Fern (*Cyclosorus interruptus*)	Langmuir model (46.25 mg/g)	Pseudo-second order	Zhou et al. [32]
	Yeast (*S. cerevisiae*)	Langmuir isotherm	Pseudo-second-order	Amirnia et al. [17]
Methylene blue	Giant duckweed (*Spirodela polyrrhiza*)	Langmuir model	First order	Waranusantigul et al. [2]

4.4.4 Evaluation of Equilibrium Binding of Metals

The biosorption process involves a solid phase, biosorbent and a liquid phase, solvent, normally water containing a dissolved species to be sorbed. Due to the higher affinity of the sorbent for the metal species, the latter is attracted to the solid and bound by a number of different mechanisms. This process continues until equilibrium is established between dissolved and solid-bound sorbate (at a residual, final

or equilibrium concentration C_f). The affinity of the biosorbent for the metal determines its distribution between the solid and liquid phases. The quality of the sorbent material is based on the number of metals it can attract and preserve in an immobilized form. The determination of the metal uptake (q) by the biosorbent is most often based on the material balance of the sorption system: metal that disappeared from the solution must be in the solid. The sorption uptake, q, can be expressed in different units depending on the purpose of the application: for example, milligrams of metal sorbed per gram of the (dry) sorbent material (the basis for engineering process-mass balance calculations), or mmol g21 or meq g21 (when stoichiometry and/or mechanism are considered). For biosorption process scale-up and applications, the uptake expressed per unit (reactor) volume is also important [17].

4.4.5 *Comparison of Sorption Performance*

To examine the performance of different biosorbent, the uptake of metal by those two must be compared only at the same equilibrium concentration as the illustration (Fig. 4.4) which one comparison at low C_f (e.g., 10 mg/L) and another at high C_f (e.g., 200 mg/L) [17]. The comparison of single metal sorption performance is best based on a complete single-sorbate sorption isotherm curve derived under the same environmental conditions, pH, temperature, ionic strength for example. Sorption

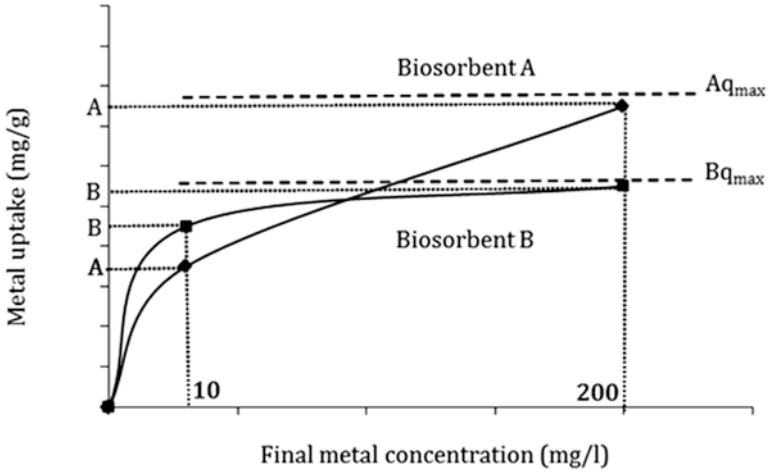

Fig. 4.4 Biosorption equilibrium-isotherm plots of metal uptake (q) against the residual (metal) concentration in the solution. Different biosorbents, A and B, are being compared. Biosorption performance in terms of uptake (q_{10}, q_{200}) has to be ruled on the same equilibrium (final) metal concentration, e.g., 10 and/or 200 mg/L. Reproduced from Kratochvil D., Volesky B. 1998. Advances in the biosorption of heavy metals. Trends. Biotechnol. 16:291–300 [17], with permission of Elsevier

isotherms are plots of the sorption uptake (q) and the final equilibrium concentration of the residual sorbate remaining in the solution (C_f).

$$q = q_{\max} \frac{bC_f}{1 + bC_f}$$

$$q = KC_f^{1/n}$$

These models do not reflect any mechanisms of metal uptake but reflecting the experimental curves. Ion exchange processes apparently play an important role in biosorption, and this is reflected in correspondingly different equilibrium models proposed for biosorption based on ion-exchange principles [17]. Langmuir isotherm is being widely used although it does not match up to the biosorption. It incorporates two easily interpretable constants: $q_{\max}$, which corresponds to the highest possible metal uptake and coefficient b, which is related to the affinity between the biosorbent and metal. Low values of b are reflected in the steep initial slope of a sorption isotherm, indicating an appropriate high affinity. Accordingly, the high quality biosorbent is one with a high $q_{\max}$ and a steep initial sorption isotherm slope (low b). Rangsayatorn et al. [25] have shown that alginate immobilized cell of *Spirulina platensis* was a better biosorbent than silica immobilized cells since $q_{\max}$ of alginate and silica immobilized cell was 70.92 and 36.63 mg Cd/g dry weight, respectively, while the binding constant (b) was 0.071 and 0.196, respectively (Fig. 4.5).

When the sorption equilibrium is established, the metal immobilized in the biosorbent will be in equilibrium with the residual concentration of metal in the liquid solution. As a consequence, the initial concentration of the metal (C_i) is of little significance to the batch sorption-equilibrium tests that can simply be seen. It can be used to identify the final concentration range which also depends on the amount of biosorbent (S) in the system. It should also be noted that in the result of the experiment there is very little control over the value of C_f−. This value is subsequently used for the uptake q calculation from the metal mass balance in the system with solution volume V:

$$q = \left(C_i - C_f\right)\frac{V}{S}$$

Therefore, it is necessary to consider both the uptake and removal efficiency when evaluating biosorbent potential. The uptake is an important parameter often used to characterize the performance of a biosorbent in a packed column. The comparison of biosorbent performance based on removal percentage is often used in the collected works which can be calculated as follows:

$$\text{Removal efficiency}\,(\%) = \frac{m_{\text{ad}}}{C_0 F t_e} \times 100$$

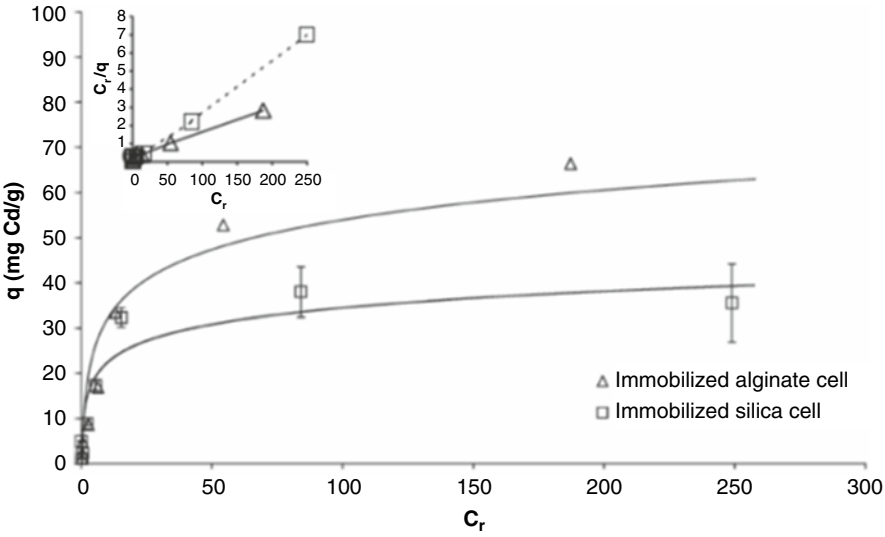

Fig. 4.5 Langmuir isotherm biosorption of *Spirulina platensis* immobilized on alginate gel and silica gel. To calculate q_{max}, the Langmuir equation was rearranged as $\frac{C_f}{q} = \frac{C_f}{q_{max}} + \frac{1}{b.q_{max}}$, the linear transformation of which is shown in the inset. Reproduced from Rangsayatorn N., Pokethitiyook P., Upatham E.S., Lanza G.R. 2004. Cadmium biosorption by cells of *Spirulina platensis* TISTR 8217 immobilized in alginate and silica gel. Environ. Inter. 30:57–63 [25], with permission of Elsevier

where C_0 and F are the inlet solute concentration (mg/L) and flow rate (L/h), respectively. It is important to note that the removal efficiency in biosorption column is independent of the biosorbent mass, but exclusively dependent on the flow volume. The column uptake (Q_{col}) can be calculated by dividing the total mass of biosorbed sorbate (m_{ad}) by that of the biosorbent (M). The mass of biosorbed metal is calculated from the area above the breakthrough curve (C vs. t) multiplied by the flow rate.

The slope of the breakthrough curve from t_b to t_e (dc/dt) is often used to characterize the shape of the curve [54]. The overall performance of flow-through columns is strongly related to the length and shape of the ion exchange zone that develops during sorption and regeneration (Fig. 4.6).

This zone develops between the section of the column that is saturated with metal(s) and the section that still contains fresh biosorbent. The breakthrough point is the time (t_b) when the metal shows up in the effluent stream at some determined concentration. The time t_e is the time when the whole column sorption bed becomes totally saturated by the metal at its inflow concentration and the bed is no longer effective. The time interval between t_b and t_e relates to the length of the mass-transfer zone in the column bed. The fact that actual mass-transfer zones achieve S-shaped is attributable to adsorption mechanism and mass transport conditions. It is preferential with an extended breakthrough curve with a steep slope, by means of a shorter

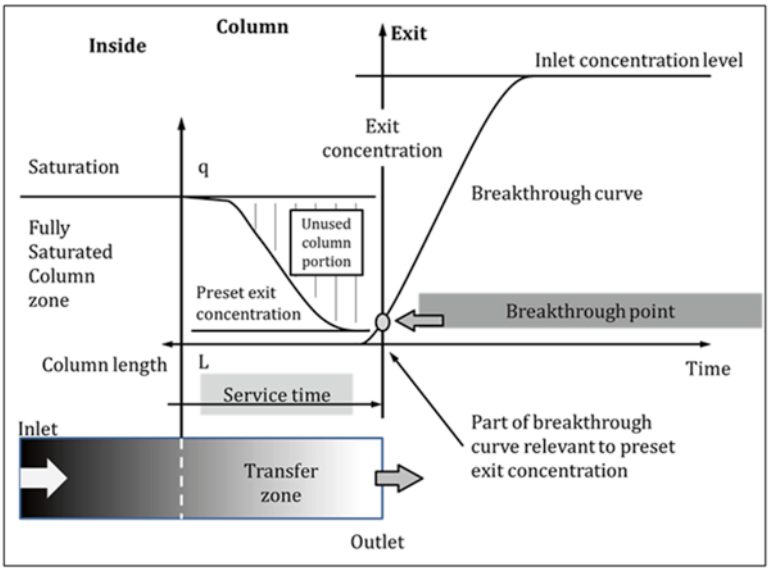

Fig. 4.6 Breakthrough point in a flow-through packed-bed biosorption column. When the metal "breaks through" and becomes detectable at the column exit at a given concentration, the column service time is over. Reproduced from Volesky B. 2003. Biosorption process simulation tools. Hydrometallurgy. 71:179–190 [47], with permission of Elsevier

mass transfer zone, which implies a longer column facility time and greater utilization of the biosorbent portion inside the column [17]. Thus, for effective biosorbents, a delayed breakthrough, earlier exhaustion, shortened mass transfer zone, high uptake, steep breakthrough curve, and high removal efficiency would be expected [7]. However, this is an estimation that could lead to complete misrepresentative conclusions on the relative sorption performance. It can only serve the purpose of basic coordination for the fast and fairly accurate screening of biosorbent materials [17].

A number of parameters can be used to characterize the performance of packed bed biosorption, including the length of the sorption zone, uptake, removal efficiency, and slope of the breakthrough curve [50, 54]. A mass transfer zone will develop between the gradually saturated section of the column and the fresh biosorbent section [55]. The length of this zone is important practically, which can be calculated from:

$$Z_m = Z\left(1 - \frac{t_b}{t_e}\right)$$

where Z denotes bed depth (cm), and t_b and t_e the column breakthrough and exhaustion times (h), respectively. A very important practical consideration arises from the affinity of different sorbates for the sorbent material. For the case of a

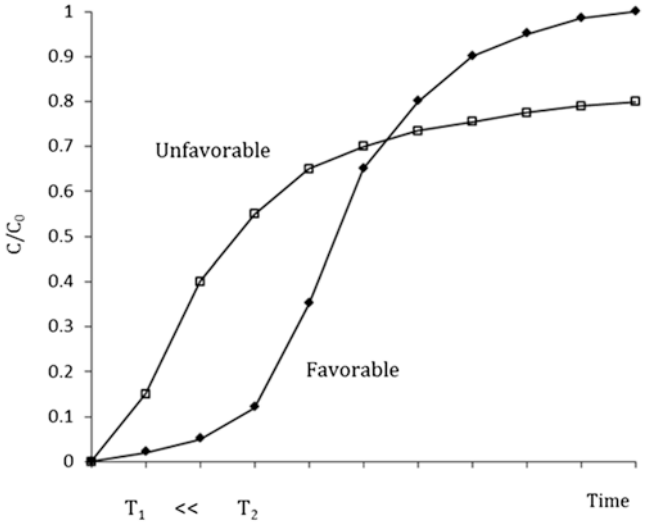

Fig. 4.7 Breakthrough curves obtained from operation of biosorption columns. An unfavorable breakthrough curve is flat and trailing, indicating a wasteful long transfer zone inside the column. A favorable breakthrough curve, on the other hand, is steep and sharp, showing the effective utilization of the biosorbent material inside the column. Reproduced from Kratochvil D., Volesky B. 1998. Advances in the biosorption of heavy metals. Trends. Biotechnol. 16:291–300 [17], with permission of Elsevier

species A sorbing onto B-saturated biosorbent, the theory of ion exchange separates between two different states of column performance, depending on the respective affinities of A and B for the sorbent material. These two states are reflected in the shapes of the breakthrough curves resulting from such column operations (Fig. 4.7).

If species A is more strongly bound to the biosorbent than species B, then the short zone develops in a column and maintains its shape as it moves down the column, on the other hand, if the affinity of B is greater than that of A, the zone extends across a large section of the column and is susceptible to extending as it moves along the column during the operation time. This indicates that a high degree of biosorbent utilization or regeneration is achieved only if the species sorbing onto a biosorbent has a higher affinity than the one used for presaturating the sorbent material. For that reason, the selection of both the ionic form of the biosorbent for the loading stage and the regenerant for the regeneration stage should follow the pattern of strongly binding A replacing weakly bound B [17].

4.5 Application of Biosorption: Packed Bed Column Continuous Flow Studies

Packed bed experiment was conducted at room temperature (25 ± 2 °C) in a 1-cm ID glass column, packed with 0.5 and 1 g of *Hydrilla verticillata* dry biomass to obtain bed volumes of 3 and 4.3 mL, respectively [33]. The results showed that a fixed-bed column packed with *H. verticillata* biomass designed to operate as a continuous liquid flow system for Cd biosorption was operational. Fixed-bed breakthrough curves at two different weights of dry biomass (0.5 and 1 g) were obtained to illustrate the capability of column operation (Fig. 4.7). The packed bed column could purify 10 mg/L Cd solution even below the detection limit of 0.02 mg/L before the breakthrough occurred at both weights used. The column containing 1 g of dry weight of the biomass removed 10 mg/L Cd solution to below the detection limit of 0.02 mg/L before the breakthrough occurred (Fig. 4.8). Regeneration of the biosorbents was also possible for at least three cycles as shown in Table 4.4.

Despite some existing limitations in biosorbent selection and usage. Biosorption of heavy metals from the aqueous solution is one of the most promising and alternative techniques for the removal of heavy metals from aqueous solutions.

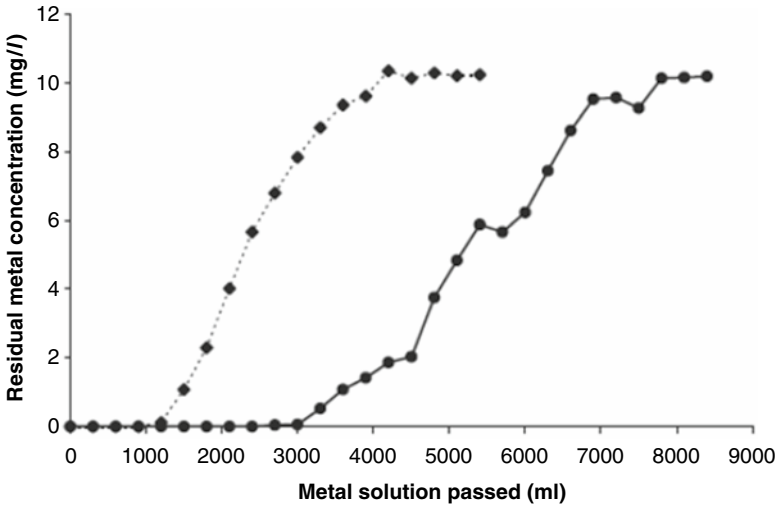

Fig. 4.8 Biosorption of Cd in fixed-bed column with continuous flow at different sorbent biomasses. Conditions: initial Cd concentration 10 mg/L; pH5; actual flow rates 10.91 mL/min for 0.5 g and 9.88 mL/min for 1 g; 25 ± 2 °C. *Symbols*: diamonds, 0.5 g of biomass; circles, 1 g of biomass

Table 4.4 Adsorption-desorption of Cd by *Hydrilla verticillata* dry biomass packed column using 0.1 M HCl as desorbing agent

Dry biomass (g)	Cycle	Cd adsorption (%)
1	1	100
	2	100
	3	95.62
2	1	100
	2	85.04
	3	98.32
3	1	100
	2	94.31
	3	80.29

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