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Heavy Metal Removal by Microbial Biosorbents

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Abstract Conventional methods for heavy metal removal are precipitation, coagulation, reduction, ion exchange, evaporation, and membrane processes. This chapter describes the use of microbial biosorbents in removing heavy metals. Environmental factors, mechanisms, and isotherms of biosorption were discussed. Biosorption kinetics includes pseudo-first-order, pseudo-second-order, and Elovich kinetics model.

1. INTRODUCTION

Due to the rapid industrialization, an alarming amount of toxic heavy metals has been released into the environment endangering natural ecosystems and public human health. Also, due to their mobility in natural water ecosystems and their toxicity to higher life forms, heavy metal ions in waste water and ground supplies have been regarded as major inorganic contaminants in the environment. Hundreds and thousands of tons of heavy metals are discharged from electric battery manufacturing, electroplating, refining process, internal-combustion engines fueled with leaded petroleum, mill tailings, landfill run off, and mining activities. Even if they are present in dilute, undetectable quantities, they are hazardous through natural processes such as biomagnification, concentrations may become elevated to such an extent that they begin exhibiting toxic characteristics. Heavy metals act on the central nervous system, kidney and liver damage, renal disturbances, lung insufficiency, bone lesions, cancer, and hypertension in humans. Elements such as lead and cadmium exhibit human toxicity at extremely low concentrations. The elements silver, chromium, copper, and zinc

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also exhibit toxic properties to human although the concentrations are orders of magnitude higher than that required for Cd or Hg toxicity.

Conventional methods for heavy metal removal are precipitation, coagulation, reduction, ion exchange, evaporation, and membrane processes. These methods have several disadvantages such as less effective removal of metal ion, high reagent requirements, high costs, the generation of toxic sludges, and the problem of the safe disposal of the materials (1). Biosorption (biological metal removal) process has distinct advantages over conventional methods, for example, highly selective, more efficient, easy to operate, and cost effective.

The potential for using microorganism in the treatment of metal-bearing wastewater has been studied intensively and many microorganisms including bacteria, fungi, and algae have been found to remove metals from solutions (2, 3). The biosorption of heavy metal ions by microorganisms may be placed into two categories: (a) metabolism-independent entrapment in the cellular structure and subsequent sorption on to the binding sites present in the cellular structure and (b) metabolism-dependent transport across the cell membrane through the cell metabolic cycle (4). The metal-sorption mechanisms including complexation, ion exchange, coordination, adsorption, chelation, and microprecipitation are complex and dependent on the chemistry of the metal ions, surface properties of the microorganisms, and cell physiology (5, 6). The biosorption process is affected by physico-chemical influence of the environment, such as pH, temperature, biomass concentration, initial metal concentration, and competing ion (7).

Biosorption of heavy metals is affected by many experimental factors such as pH, ionic strength, biomass concentration, temperature, and presence of different metallic ions in solution. The variability of these factors in real wastewaters makes it necessary to know how they influence biosorption performance. As a consequence of these possible multiple interactions the comprehension of biosorption phenomena is very complex and requires a study of both the solution chemistry of metal ions (depending on pH, anions and/or ligands in solution) and the mechanisms of passive metal uptake (ion exchange, complexation, microprecipitation, etc.) (7).

In order to develop an effective and accurate design model for adsorption systems, adsorption kinetics and equilibrium isotherm data are two of the most important parameters to understand. Kinetic analyses not only allow estimation of sorption rates but also lead to suitable rate expressions characteristic of possible reaction mechanisms. The calculated kinetic parameters can be of a great practical value for technological applications since kinetic modeling successfully replaces time and material consuming experiments A majority of research for sorption rate model has been based on a reaction kinetic sorption process in which reaction rate constants are determined as the key parameters describing the process (8, 9).

Biosorption phenomena occur as a result of metal ion interactions with functional groups in various functional groups on the cell surface. It is believed that phosphate, carboxyl, amine, and amide groups found in carbohydrates, lipids, proteins, and other biopolymers of the microbial cell envelope represent the main sites for metal adsorption (10). The charge distribution and geometry of these binding sites may vary with the composition of the cell envelope of each microorganism, resulting in markedly different metal-binding affinities.

2. CONVENTIONAL TECHNOLOGIES FOR HEAVY METAL REMOVAL

Metal removal or recovery processes are carefully considered not only toxic heavy metal removal in environmental aspects, but also precious metal recovery in industrial aspects. Those metals considered environmentally hazardous, or which are of technological importance, strategic significance or economic value must be removed or recovered at their source using appropriate treatment systems. Although many processes for heavy metal removal/recovery have been studied, more efficient process are needed for recycle of water, strict regulation for the effluent concentration of heavy metals, and the reduction of operating cost. Each treatment process has their own advantages and disadvantages and to know these factors is useful for selection and application to the specific case. Brief considerations of conventional metal treatment processes are as follows.

2.1. Chemical Precipitation

The most widely used process for removal of heavy metals from solution is chemical precipitation. The conventional process of heavy metal removal from industrial wastewater involves chemical precipitation of metals usually by lime, followed by settling of the metal precipitates in a pond and/or a clarifier. The most commonly used precipitation technique is hydroxide treatment due to its relative simplicity, low cost of precipitant, and ease of automatic pH control. Hydroxide precipitates tend to resolubilize if the solution pH is changed, but the removal of mixed metal wastes may not be effective because the minimum solubilities for different metals occur at different pH condition. Carbonate precipitation and sulfide precipitation has also been used for the treatment of metal containing waste water. Generally, precipitation has been widely used for its simplicity, but has two drawbacks: it usually results in a net increase in the total dissolved solids of the wastewater being treated, and large amount of sludge requiring treatment, which, in turn, may contain toxic compounds that may be difficult to treat (11).

2.2. Ion Exchange

Ion-exchange resins have recently found a niche in the market of water and waste-water treatment. Also, they are an effective means of removing heavy metals from wastewater. When the resins are saturated, they must be regenerated with an acid or alkaline medium to remove the metal ions from the resin bed. Due to the fact that ion exchange is efficient in removal of dissolved solids from normally dilute spent rinse waters, it is well suited for use in water purification and recycles. Ion exchange may be capable of treating for high purity heavy metal solution and sequential operation. However, it requires pretreatment process to reduce suspended solid concentration in solution to prevent fouling or channeling. However, apart from their cost, which can be prohibitive especially to smaller processing plants, resins are vulnerable to oxidation by chemicals, are affected by the presence of magnesium or calcium ions in solution, and are prone to fouling by precipitates and organics (12).

2.3. Membrane Technology

The use of membrane technology for valuable metal removal is gaining considerable attention in many industries. The ultrafiltration can be used to remove water from wastewater containing emulsified oil, and exclude the metal particles. However, ultrafiltration membranes need to be cleaned and backflushed regularly to operate efficiently and replaced periodically. Reverse osmosis (RO) may be applied in plating processes removing sodium chloride. RO system requires high-quality feed for efficient operation, thus wastewater must be treated to remove solids prior to RO treatment. Application of membrane technology to metal-bearing waste streams has several major drawbacks. Apart from the expense, membranes are also unable to resist certain types of chemicals and pH values and are prone to deterioration in the presence of microorganisms. Membrane fouling, compaction, scaling, limited life of membranes, dissolution of the membrane by oxidized agents, solvents and other organic compounds, and applicability only to feed streams with low concentrations of metal ions are major limitations associated with the use of membrane technologies.

2.4. Flocculation and Coagulation

The coagulation–flocculation processes facilitate the removal of suspended solids, colloidal particles. It is used in the final stage of solids–liquids separation. Coagulation is the destabilization of colloidal particles brought about by the addition of a chemical reagent called coagulant. Flocculation is the agglomeration of destabilized particles into microfloc and after into bulky floccules that can be settled called floc. The addition of another reagent called flocculant or a flocculant aid may promote the formation of the floc. Flocculation is the slow stirring or gentle agitation to aggregate the destabilized particles and form a rapid settling floc. This technique has been known to be capable of removing heavy metals from solution. EPA investigated the use of lime softening and coagulation (using ferric sulfate or alum) for removal of heavy metals as Pb^{2+}, Cd^{2+}, Cr^{3+}, Cr^{6+}, etc (13).

2.5. Flotation

Flotation, nowadays, is considered a well-established unit operation in the field of mineral and environmental technology. It also has been practiced for the separation of biological materials, such as algae from drinking water sources, mainly due to their small size and density. Flotation, following metal biosorption, was proved to be a useful and effective separation method of metal-loaded biomass, producing efficient removals, usually over 95%. The main critical parameters are solution pH and ionic strength. The different techniques, such as foam or bubble fractionation, foam separation or froth flotation, were examined for the separation of metal-loaded baker's yeast *Saccharomyces cerevisiae* (14).

2.6. Electrodialysis

Electrolytic metal recovery is one of a number of technologies capable of removing metals from wastewater. Electrolytic industrial processes for metals include the production of metals themselves from their compounds, which is called the electrowinning of metals; the electrolytic purification of metals; and the deposition or electroplating of metals on conducting

surfaces. In all three types of electrolytic process, the reactions are reduction of ions of the metal in solution in some carefully selected electrolyte. This process is a highly energy-dependent and labor-intensive process. Electrodialysis is a process that efficiently maintains a low metal ion concentration in the anodizing bath solution by transporting metal ions from the bath solution through a selective membrane into a capture media using an electrical current to induce flow. In the electrodialysis process, ionic components of a solution are separated through the use of semipermeable ion-selective membranes. However, this process is moderately high capital cost, increase in the number of possible exposures with regard to the handling of hazardous waste, and must be able to locate company that will recover and reclaim metals from the sludge.

The conventional approaches to heavy metal removal mentioned above are summarized in Table 12.1.

Table 12.1
Conventional metal removal technologies

Method	Disadvantage	Advantage
Chemical precipitation	pH dependence Difficult separation Adverse effect by complexing agent Resulting sludges Chemicals required	Simple and chip
Ion exchange	Sensitive to particles High operational cost No selectivity to alkaline metals Metallic fouling	No sludge generation Pure effluent metal recovery possible
Membrane	Membrane fouling Limited life of membrane Expensive High pressure	Pure effluent
Flocculation Coagulation	Chemicals required (electrolytes) Depend on basin design	Generate very fine particles of precipitates
Flotation	Less selective for heavy metals	Cost competitive to precipitation
Electrodialysis	Takes time Large electrode surface area required Fouling Expensive	Metal Selective

3. HEAVY METAL REMOVAL BY MICROBIAL BIOSORBENTS

3.1. Biosorption

The conventional heavy metal removal processes have several disadvantages such as less effective removal of metal ion, high reagent requirements, high costs, the generation of toxic sludges, and the problem of the safe disposal of the materials (1). Compared with conventional methods for removal of toxic heavy metals, biosorption process offers the advantages of low cost, minimization of the volume of chemical and/or biological sludge to be disposed of, high efficiency in detoxifying very dilute effluents, and high metal selectivity. These advantages have served as the primary incentives for developing biosorption processes to treat waste water contaminated by toxic heavy metals. Also the increasing demand for eco-friendly and economical technologies has led to the search of low-cost alternatives for heavy metal treatment. In this light, biological materials have emerged as an eco-friendly and economic option. The advantages of biosorption are as follows.

- *Cost effective*. The cost for biosorbents is low since often they are made from abundant natural source or waste biomass from industry.
- *Metal selective*. The metal sorption capacity of different types of biomass can be more or less selective on different metals. This depends on various factors, such as type of biomass, mixture in the solution, type of biomass preparation, and physico-chemical environment.
- *Regenerative*. Biosorbents can be reused after the metal is recycled. Some types of biomass are immobilized in a synthetic polymer matrix to obtain the required mechanical propertied for repeated reuse.
- *Minimization of sludge generation*. No secondary problems with sludge occur with biosorption, as is the case with many other techniques such as precipitation.
- *Metal recovery possible*. Metal can be recovered after being sorbed from the solution by desorbing solutions such as acid and chelate agents.
- *Competitive performance*. Biosorption is capable of a performance comparable to the most similar technique, ion exchange treatment.

Biosorption is a process that utilizes inexpensive dead biomass to sequester toxic heavy metals. Biosorbents are prepared from the naturally abundant and/or waste biomass from industrial use. The potential for using microorganism in the treatment of metal-bearing wastewater has been studied intensively and many microorganisms including bacteria, fungi, and algae have been found to remove metals from solutions (2, 3). Microbial biomass can passively bind large amounts of metals, a phenomenon commonly referred to as biosorption, thus providing a cost-effective solution for industrial wastewater management.

The biosorption of heavy metal ions by microorganisms may be placed into two categories: (a) metabolism-independent entrapment in the cellular structure and subsequent sorption on to the binding sites present in the cellular structure (biosorption) and (b) metabolism-dependent transport across the cell membrane through the cell metabolic cycle (bioaccumulation) (4). However, bioaccumulation is mediated only by living biomass. Further, bioaccumulation is a growth-dependent process and it is difficult to define a variety of effluents in contrast to biosorption which is growth independent. Thus, microbial biomass can be used and exploited more effectively as biosorption rather than bioaccumulation.

Table 12.2
Microbial biosorbents for the removal of heavy metals

Yeast & Fungi	Bacteria	Algae
Aspergillus niger	*Arthrobacter globiformis*	*Ascophyllum nodosum*
Aureobasidium pullulans	*Arthrobacter simplex*	*Chlorella vulgaris*
Cladosporium resinae	*Arthrobacter viscosus*	*Clodophara crispata*
Ganodoma lucidum	*Bacillus subtilis*	*Durvillea potatorum*
Penicillium chrysogenum	*Escherichia coli*	*Ecklonia maxima*
Penicillium digitatum	*Micrococcus luteus*	*Fucus vesiculosus*
Phanerochaete chrysoporium	*Pseudomonas aeruginosa*	*Lessonia flavicans*
Rhizopus arrhizus		
Rhodotorula aurantiaca	*Pseudomonas fluorescens*	*Sargassum filipendula*
Rhodotorula glutinis	*Pseudomonas syringae*	*Sagassum fluitans*
Rhodotorula rubra	*Streptomyces longwoodensis*	*Sargassum natans*
Saccharomyces cerevisiae	*Streptomyces niveus*	*Sargassum vulgare*
	Streptomyces noursei	
	Zoogloea ramigera	

Biosorption is a rapid phenomenon of passive metal sequestration by the nongrowing biomass (15). The binding capacities of certain biomass are comparable with the commercial synthetic cation exchange resins. Biosorption mainly involves cell surface complexation, ion exchange, and microprecipitation. Different microbes have been found to vary in their affinity for different heavy metals and, hence, differ in their metal-binding capacities. Some biomass exhibit preference for certain heavy metals, whereas others do not show any specific binding and are broad range.

3.2. Microbial Biosorbents

Microbial biomass types have been investigated for their biosorptive potential that include bacteria, yeasts, filamentous fungi, and marine algal (12, 16–20). The reported microbial biosorbents are listed in Table 12.2.

Certain biomass types are evidently more suitable than others to a specific application. The affinity that a biosorbent material exhibits for a specific metal cation will dictate the practicality of its implementation for remediation of a particular waste stream.

Among micro-organisms, fungal biomass offers the advantage of having a high percentage of cell wall material, which shows excellent metal-binding properties. Many filamentous fungi and yeast have shown an excellent potential of metal biosorption, particularly the genera *Rhizopus*, *Aspergillus*, *Streptoverticillum, Penicillium, Rhodotorula*, and *Saccharomyces* (21–26).

Of the species studied, fungi have been studied extensively, partly because of the wide range of morphological types they possess and availability of large amounts of fungal biomass and products derived from industrial processes and fermentations (27). Fungi are able to remove heavy metals from waste water in rather substantial quantities. In certain instances, biosorption of heavy metals by fungal cells has been observed to be more than that of conventional

adsorbents such as activated carbon and ion-exchange resins. Among fungi, *Rhizopus* sp. and *Aspergillus* sp. have been studied extensively as biosorbent for a variety of heavy metals. *Penicillium chrysogenum* showed the ability of gold biosorption from a cyanide solution although the capacity was not encouraging.

Yeasts possess an acknowledged potential for removal of heavy metal cations (29, 30). Yeasts are used in a variety of industrial fermentation processes and can be easily cultivated using unsophisticated fermentation techniques and inexpensive growth media. Yeasts cultures are also amenable to genetic and morphological manipulations, which may result in better raw biosorbent material. Among yeasts, heavy metal biosorption by *Saccharomyces cerevisiae* has been most studied (31, 32). In particular, this yeast is a reasonably potent biosorbent material for cadmium. It was recently reported that some soil yeasts including *Rhodotorula* sp. were resistant to heavy metal toxicity and have shown to play a role in processes of mineral cycling (26, 32, 33). Cho et al. reported that *R. glutinis* and *R. aurantiaca* showed the high capacity of biosorption for lead (23, 24). *Rhodotorula* sp. also has an aptitude for degradation of cyano-metals and bioleaching of mineral-containing metals (34, 35).

There are reports on the biosorption of metal using bacteria such as *Pseudomonas* sp., *Zoogloea ramigera*, *Streptomyces* sp., and *Arthrobacter* sp. (7, 17, 36). Among bacteria, *Bacillus* sp. has been identified as having a high potential for metal sequestration and has been used in commercial biosorbent preparation (37). The members of this genus are easy to culture and have shown high tolerance to heavy metal toxicity. *Zoogloea ramigera* has long been considered the typical activated sludge bacterium responsible for the formation of activated sludge flocs. Immobilized *Zoogloea* was shown to have a high adsorption capacity for Cu and Cd ions.

There are many reports on the biosorption of heavy metals by marine algae such as *Sargassum* sp., *Ascophyllum* sp., and *Chlorella* sp. (6, 38). Marin algae offer advantages for biosorption due to bulk availability of their biomass from water bodies and their macroscopic structures. Thus, marine algae became the candidate for the alternative biosorbents. *Sargassum* seaweed in this group has shown very high biosorptive capacities for various metals (39). In brown algae *Sargassum* biomass, alginate in the cell wall is the main component responsible for the heavy metal sorption.

3.3. Environmental Factors for Biosorption

In metabolism-dependent biosorption, cell wall structure and the metabolic state of the cell depend on substrate composition, thus growth in different media should influence the capacity and selectivity of metal uptake by creating other binding sites or diverse enzymatic system within the cell. The use of living cells for the biosorption of heavy metals has the disadvantage in nutrient requirements, metal toxicity, and cell death system failure. Thus, the control of environmental factors affecting the biosorption of living cell is a more complicated and tedious procedure.

It was reported that dead microbial cells are able to remove heavy metal ions from metal-laden wastewater. The biosorption technology is the passive method of metal removal by dead biomass. The dead (metabolically inactive) biomass of a variety of microorganism have been shown to produce effective biosorbents. The use of dried biomass as biosorbents mainly

depends on chemical mechanisms involving the interactions of metal ions with functional groups that are native to the proteins, lipids, and carbohydrates (especially polysaccharides) associated with the cell wall surface.

Some methods of killing cells (physical methods such as drying, heat treatment and chemical methods such as acidic, caustic, organic treatments) may actually improve the biosorption properties of the biomass. Aksu and dönmez (40) reported that the heat treatment method (drying) increased the biosorption capacity of the *Candida* biomass by 91.9% as compared with that of untreated biomass. They suggested that the enhanced sorption capacity could be attributed to more complex actions taking place on the surface, such as the formation of electrostatic bonds, change in the overall surface charge, and modification of binding sites.

Biosorption of heavy metals is affected by many experimental factors such as pH, ionic strength, biomass concentration, temperature, and presence of different metallic ions in solution. The variability of these factors in real wastewaters makes it necessary to know how they influence biosorption performance. As a consequence of these possible multiple interactions the comprehension of biosorption phenomena is very complex and requires a study of both the solution chemistry of metal ions (depending on pH, anions, and/or ligands in solution) and the mechanisms of passive metal uptake (ion exchange, complexation, microprecipitation etc.) (7).

A very rapid biosorption suggests that biosorption is typical for sorption of metals involving no energy-mediated cell surface binding. Rapid sorption of metal by the biosorbent is desirable providing for a short solution-biosorbent contact time in the actual process (41).

The ability of microbial biomass to bind metals in solution has been shown to be a function of pH. For example, change of less than 1 pH unit results in an increase in the amount of metal adsorbed from almost 0 to 100% (42, 43). The solution pH affects both the solubility of metals and the ligands responsible for binding of metal ions at the cell wall (44). The metal biosorption depends on the protonation or deprotonation of the cell wall functional groups. At low pH, the concentration of protons is so high that metal binding sites become positively charged and metal cations and protons compete for binding sites, which results in lower sorption of metal. With an increase in pH, the functional groups on the cell wall with negative charge increase due to deprotonation of the metal binding sites, which promote the metal sorption. The optimal pH value for adsorption of metal ions varies with the type of biomass and metal ions. pH between 4.0 and 8.0 is widely accepted as being optimal for metal sorption for almost all types of biomass (30, 45).

The biomass concentration is an important factor that determines the extent of metal biosorption from solution. It was reported that higher specific sorption at lower biomass concentrations could be due to an increased metal to biosorbent ratio (46). It was suggested that with increasing biomass concentration there is an increase in electrostatic interactions between cells and this causes the cells to agglomerate, which contribute to a decrease in the amount of binding sites available. However, Fourest and Roux (44) reported that the reduction in metal sorption with increasing biomass concentration is due to an insufficiency of metal ions in solution with respect to available binding sites.

Temperature changes in biosorption of metal affects the stability of the metal species initially placed in solution and microorganism–metal complex (47). In the case of metabolically inactive biosorbents, the dependence of capacity on temperature change can be negligible (48, 49). In contrast, biosorption of Cr(VI) by *Rhizopus niglicans* and lead (II) removal by *Zoogloea ramigera* showed endothermic nature (7, 50).

It is well known that the presence of some competing ions such as calcium, magnesium, sodium, and potassium can affect the sorption of heavy metal ions to biomass and reduce the binding capacity to some extent (49, 51). Schiewer (52) was reported that the electrostatic attraction only influenced the binding of light metal on biomass. According to his report, when heavy metal cation binding by marine algae *Sargassum* biomass is tested under the presence of Na^+ ion, Na^+ binding can be neglected unless present at high concentrations since it only binds weakly through electrostatic attraction and does not compete significantly with the binding of metal and proton. Since Na^+ is only bound electrostatically, it can only compete or interfere with the electrostatic (not covalent) binding of protons and divalent metal ions.

3.4. Biosorption Mechanisms

The complexity of the cell wall structure implies that there are many ways for the biosorption of heavy metals by microorganisms. Therefore, biosorption mechanisms are various and in some cases they are composed of more than one mechanism. However, the biosorption mechanisms are not completely understood. The biosorption mechanisms are summarized in Figs. 12.1 and 12.2.

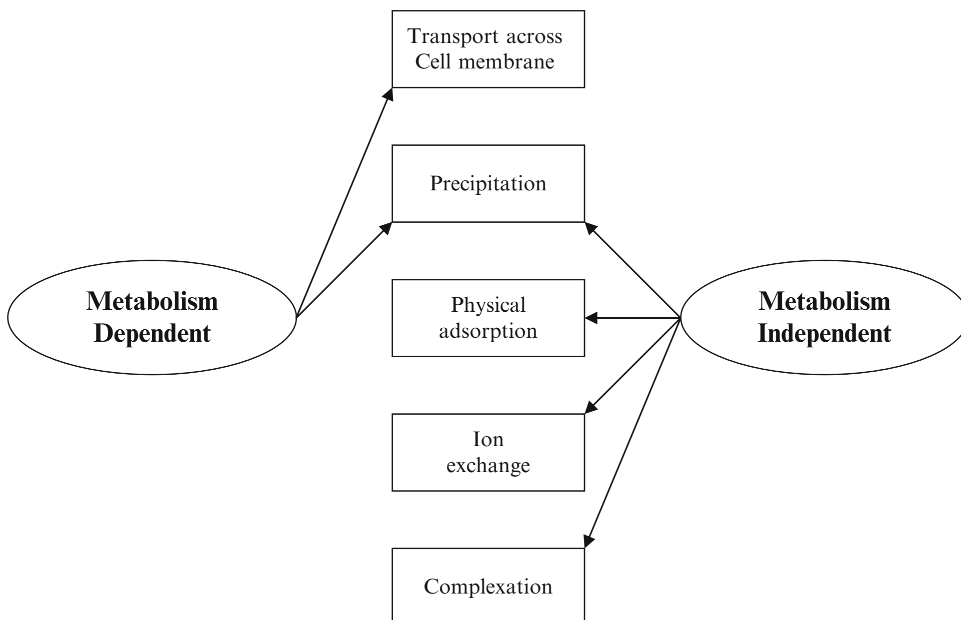

Fig. 12.1. Biosorption mechanisms according to the dependence on the metabolism of cells.

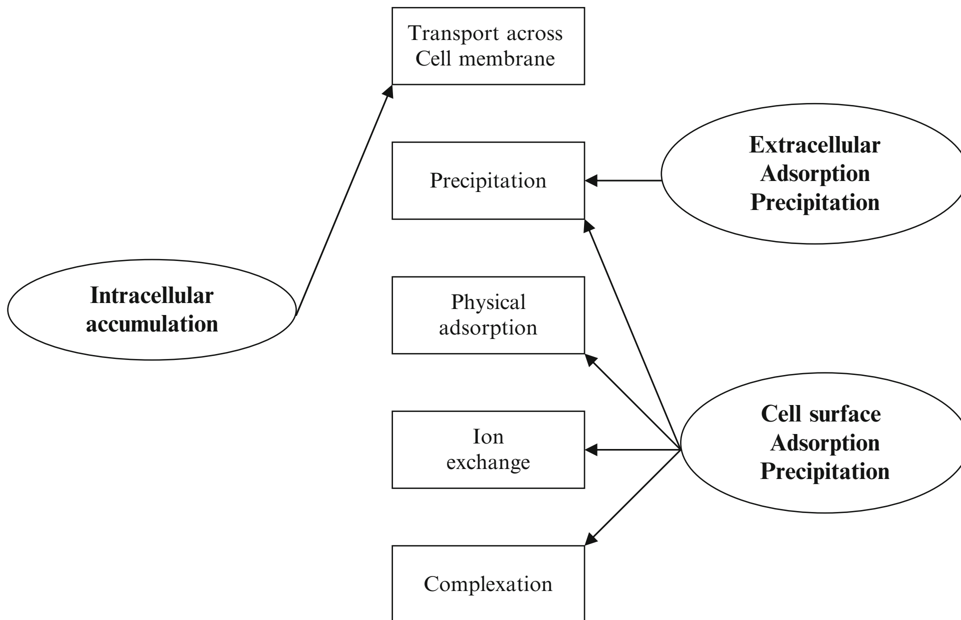

Fig. 12.2. Biosorption mechanisms according to the location where the metal removed is found.

According to the dependence on the cell's metabolism, biosorption mechanisms can be divided into two categories (53):

1. *Metabolism dependent* (*active metal uptake, bioaccumulation*). Transport across cell membrane, precipitation. It is an energy-driven process.
2. *Metabolism independent* (*passive metal uptake, biosorption*). Precipitation, physical adsorption, ion exchange, complexation.

Dead cells sequester metals through chemical functional groups of the material comprising the cell and in particular the cell wall, which constitutes a large percentage of the cellular dry weight. Passive metal uptake is relatively rapid and can be reversible.

According to the location where the metal removed from the solution is found, biosorption may also be classified as follows (4):

1. Extracellular accumulation/precipitation may be facilitated by using viable microorganisms
2. *Cell surface sorption/precipitation*. Ion exchange, complexation, physical adsorption, precipitation can occur with alive or dead microorganisms
3. *Intracellular accumulation*. Transport across cell membrane requires microbial activity

The mechanism of biosorption is summarized as follows (41):

1. *Transport across the cell membrane*. This phenomenon is associated with cell metabolism by living biomass. This process may be mediated by the same mechanism used to convey metabolically essential ions, such as potassium, magnesium, and sodium. The metal transport system may become confused by the presence of heavy metal ions of the same charge and ionic radius (37).

2. *Complexation*. The metal biosorption from solution may take place through complex formation on the cell surface after interaction between the metal and active sites. Metal ions can bind to single ligand or through chelation. The cell surface complexation is on the concept of surface charge generated from the amphoteric surface sites, which are capable of reaction with sorbing cationic or anionic species to form surface complexes.
3. *Coordination*. The binding of metals to ligands is based on the formation of coordination compounds. The metal acts as a Lewis acid, i.e., tends to acquire enough electrons to reach an inert state, and the ligand acts as a Lewis base, i.e., has electron pairs that can be shared with the metal. Coordination, then, is a Lewis acid–Lewis base neutralization process.
4. *Ion exchange*. Ion exchange plays an important role in sorption by algal biomass and modeled the binding of heavy metal ions and protons as a function of metal concentration and equilibrium pH (52). The light metal ions presence in cell wall and membrane, such as K^+, Na^+, Ca^{2+}, and Mg^{2+} can also exchange with the metal cations.
5. *Chelation*. Chelation takes place when a ligand forms coordinate bonds with a metal through more than one pair of shared electrons, thus forming a ring structure. Depending on the requirement for electrons of the metal and the construction of the ligand, there can be a sharing of up to eight electron pairs between a single metal ion and ligand.
6. *Microprecipitation*. (Micro) precipitation may be either dependent on the cellular metabolism or independent of it. In the former case, the metal biosorption from solution is often associated with an active defense system of microorganisms. They react in the presence of a toxic metal, producing compounds which favor the precipitation process. In the case of (micro) precipitation not dependent on the cellular metabolism, it may be a consequence of the chemical interaction between the metal and the cell surface.

The physiological state of the organism, the age of the cells, the availability of micronutrients during their growth, and the environmental conditions during the biosorption process (such as pH, temperature, and presence of certain coions), are important parameters that affect the performance of a biosorbent.

3.5. Biosorption Sites

A variety of ligands located on the cell wall is known to be involved in metal biosorption (10). The main chemical groups of biomass surfaces that are capable of participating in sorption and chelation of a number of bivalent metal cations are polar or anionic in nature, such as hydroxyl, sulfhydryl, carboxyl, and phosphate, mainly those from polysaccharidic materials, which constitute most of the cell wall. The nature of the specific interactions between metal ions and biomass is quite controversial due to their complex nature and the significant number of different available binding sites for metal ions. However, the exact nature of functional groups and mechanisms responsible for heavy metal biosorption on microorganisms are not clear. The cell wall composition of various microorganisms is as follows.

Like algae, fungi also contain rigid cell walls. Although cellulose is present in the walls of certain fungi, many fungi have noncellulosic walls. The fungal cell wall presents a multilaminate, microfibrillar structure, an outer layer of glucans, mannans, or galactans and an inner microfibrillar layer, the crystalline properties of which are conferred by the parallel arrangement of chains of chitin or cellulose or noncellulosic glucan, with a continuous transition between both layers (10). The wall of a yeast cell is a remarkably thick (100–200 nm) envelope, which contains some 15–25% of the dry mass of the cell. Major structural constituents

of the cell wall are polysaccharides (80–90%), mainly glucans and mannans, with a minor percentage of chitin. Glucans (both β-2,6 and β-1,3-linked glucans are represented) provide strength to the cell wall, forming a microfibrillar network. Mannans are present as an α-1, 6-linked inner core with α-1,2- and α-1,3 side chains. Other components of the cell wall are variable quantities of proteins, lipids, and inorganic phosphate, polyphosphate, and pigments.

Fungal cell wall is composed of several layers bearing anionic groups to which metal cations bind. The adsorptive capacity of the fungal cell wall for heavy metals is determined by the structural organization of the entire protein–carbohydrate complex and by the degree of dissociation of the negatively charged functional groups and their accessibility to the metals (54).

The algal cell wall is structurally similar to the fungal cell wall. In many cases the cell wall is composed of a network generally consisting of cellulose and interspersed with amorphous materials. But it is usually modified by the addition of other polysaccharides such as pectin (highly hydrated polygalacturonic acid containing small amounts of the hexose rhamnose), xylan, mannans, alginic acids, or fucinic acid. Most of the algal cells are often covered by mucilaginous layers characterized by a significant metal sorption capacity due to the presence of uronic acids. In particular, alginic acid (linear, binary copolymer of 1,4-linked α-L-glucuronic acid and β-D-mannuronic acid) contained in brown algae shows high metal sorption capacity. Commercially important brown algae generally contain alginic acid in the range of 13–40 wt% on a dry weight basis, as a structural component of the cell wall in the form of alginates. The ability of alginate to form gels by ion exchange reaction with multivalent metal ions is a suitable property as a sorbent of heavy metals.

The functional groups responsible for the biosorption of heavy metals in the cell wall are mainly carboxyl, phosphoryl, and amine group. These functional groups provide the available binding sites of heavy metals on microorganism.

Carboxyl groups are found in abundance in cell wall attributed to organic acids, lipids, and polysaccharides. Uronic acids confer a net negative charge to the polymer and play an important role in the binding capacities of the polymer. The acidic (carboxylic) groups of uronic acid are partially ionized (carboxylate ion) in aqueous solution and these could attract and sequester metals.

Phospholipids present in the cell wall may exhibit phosphoryl groups, such as phosphatidylcholine and phosphatidylethanolamine, with minor proportions of phosphaditylinositol, phosphatidylserine, or phosphaditylglycerole, as well as sterols, mainly ergosterol and zymosterol. The yeast periplasm is a thin (35–45 Å), cell wall associated region external to the plasma membrane and internal to the cell wall. It mainly contains secreted proteins (mannoproteins) that are unable to permeate the cell wall, but fulfill essential functions in hydrolyzing substrates that do not cross the plasma membrane: invertase converts sucrose into glucose and fructose; acid phosphatase catalyzes the liberation of free phosphate from organic compounds. It was reported that the phospholipids mainly composed of phosphatidylcholine and phosphatidylethanolamine were found in the cell wall of the *R. glutinis* R-1 (55). The role of phosphomannans and carboxyl groups of cell wall protein of *Saccharomyces serevisiae* for metal binding has been identified (17). Reidl et al. (56) reported the orthophosphate extrusion in syringomycin-treated cells of *Rhodotorula pilimanae*. Polyphosphates have been

known to occur in numerous filamentous fungi and in the yeasts. In microbial cells, inorganic polyphosphate (polyP) plays a significant role in increasing cell resistance to unfavorable environmental conditions and in regulating different biochemical processes (57, 58).

Amino group is abundant in cell wall in the form of protein–peptide, protein–polysaccharide, and enzymes. Chitin and chitosan also exhibited amine group as yeast cell wall component. Chitin is a polymer of *N*-acetylglucosamine residues linked by β(1–4) glycosidic links and associated with protein in the cell walls to which it is linked via nonaromatic amino acid residues. Chitosan is produced by the deacetylation of chitin found in fungal cell walls. Chitin is found as microfibrils in the inner layer of the cell wall in the glucan matrix and mainly located in bud scars. It was reported that *Rhodotorula* sp. contained a chitin as a cell wall polysaccharide (59, 60). Kapoor and Viraraghavan (3) reported that chemically treated *Aspergillus niger* to prevent the participation of amine group in metal biosorption showed the dramatically reduction of Pb^{2+} biosorption capacity.

4. BIOSORPTION ISOTHERMS

Adsorption equilibrium may be expressed in the form of (a) a graphical or tabular record based on measurements, (b) an empirical algebraic expression fitted to the data and usually selected for its generality and simplicity of calculational use, or (c) equations based on the molecular statistics of the underlying process. Any such relationship may apply at only one temperature and is thus known as an equilibrium isotherm.

Once the adsorption process starts, it continues until equilibrium is approached between the sorbate concentrations on the solid phase and in solution. Equilibrium summons the end of the process and hence reflects the sorption capacity or affinity for a given solute.

4.1. The Langmuir Isotherm

This is proposed by Langmuir (61) for homogeneous adsorption. It assumes a uniform adsorbent surface with energetically identical sorption sites. The Langmuir formula is proposed as follows:

$$q_{eq} = q_{max} b C_{eq} / (1 + b C_{eq}), \qquad (1)$$

where q_{max} is the maximum metal sorption (mg metal/g of biomass) and b is the Langmuir isotherm constant (l/mg metal). q_{max} and b can be obtained from the linear plot of $1/q_{eq}$ vs. $1/C_{eq}$.

$$1 / q_{eq} = (1 / q_{max} b C_{eq}) + (1 / q_{max}). \qquad (2)$$

The Langmuir isotherm considers sorption as a chemical phenomenon. It was first theoretically examined in the adsorption of gases on solid surfaces. Langmuir constant b is related to the energy of adsorption through the Arrhenius equation. The higher the b, the higher is the affinity of the sorbent for the sorbate. A q_{max} can also be interpreted as the total number of binding sites that are available for biosorption, and q_{eq} as the number of binding sites that are in fact occupied by the sorbate at the concentration C_{eq}. Although the Langmuir model sheds no light on the mechanistic aspects of sorption, it provides information on uptake

capabilities and is capable of reflecting the usual equilibrium sorption process behavior. Langmuir assumed that the forces that are exerted by chemically unsaturated surface atoms (total number of binding sites) do not extend further than the diameter of one sorbed molecule and, therefore, sorption is restricted to a monolayer. In the simplest case the following *assumptions* were made:

(a) Fixed number of adsorption sites: at equilibrium, at any temperature, and gas pressure a fraction of the surface sites θ is occupied by adsorbed molecules, and the fraction $1-\theta$ is free
(b) All sorption sites are uniform (i.e., constant heat of adsorption)
(c) Only one sorbate
(d) One sorbate molecule reacts with one active site
(e) No interaction between sorbed species

Assumption of a value for the surface area covered per molecule then could allow computation of the active specific surface area of the sorbent using Avogadro's number. However, the concept of "*surface area*" cannot be used in gel-like sorbents that most biosorbents may be. As long as its restrictions and limitations are clearly recognized, the Langmuir equation can be used for describing equilibrium conditions for sorption behavior in different sorbate-sorbent systems, or for varied conditions within any given system.

Generally, the Langmuir isotherm does not describe equilibrium behavior accurately, especially with heterogeneous adsorption systems where adsorption continued beyond a monolayer. However, it is of practical importance because it is mathematically convenient and easily integrable.

4.2. The Freundlich Isotherm

The Freundlich (62) isotherm describes equilibrium on heterogeneous surfaces and, hence, does not assume monolayer capacity and takes the following form for a single component adsorption:

$$q_{eq} = K_F C_{eq}^{1/n}, \tag{3}$$

where K and n are the Freundlich constants. K related to the adsorption capacity; the larger its value, the higher the capacity. n is the adsorption intensity or the heterogeneity of the sorbent; the more heterogeneous the surface, the larger its value. Equation (3) can be linearized in logarithmic form and the Freundlich constants can be determined.

$$\log q_{eq} = (1/n) \log C_{eq} + \log K_F. \tag{4}$$

This isotherm is widely recommended due to its accuracy. It gives more accurate results than the Langmuir isotherm for a wide variety of heterogeneous adsorption systems. Though accurate and mathematically convenient, one drawback is that Freumdlich isotherm does not converge to Henry's law at low surface coverage and, therefore, fails to describe equilibria as $q \to 0$ and is thermodynamically inconsistent.

4.3. *The Redlich–Peterson Isotherm*

This is a more general formula than both Langmuir and Freundlich isotherms. The Redlich–Peterson isotherm formula is expressed by:

$$q_{\mathrm{eq}} = K_{\mathrm{R}} C_{\mathrm{eq}} \,/\, \left(1 + a_{\mathrm{R}} C_{\mathrm{eq}}^{\beta}\right), \tag{5}$$

where K_{R}, a_{R}, and β are the Redlich–Peterson constants (63). This equation can be converted to a linear form following:

$$\ln\left[(a_{\mathrm{R}} C_{\mathrm{eq}} \,/\, q_{\mathrm{eq}}) - 1\right] = \ln K_{\mathrm{R}} + \beta \ln C_{\mathrm{eq}}. \tag{6}$$

A graphical plot of the Redlich–Peterson isotherm shows that a "plateau" is reached after a continual rise in the curve, i.e., several layers of adsorption occurs first. This isotherm describes equilibrium for heterogeneous surfaces as it contains the heterogeneity factor β. It also converges to Henry's law at low surface coverage and is, therefore, thermodynamically consistent. However, it does not have as wide a practical application as the Langmuir and the Freundlich isotherms due to the inconvenience of evaluating three isotherm constants.

The illustration of the equilibrium adsorption plots and the summarized isotherm models are shown in Figs. 12.3, 12.4 and Table 12.3.

5. BIOSORPTION KINETICS

The study of sorption kinetics in heavy metal removal from wastewater is significant as it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions. Monitoring a kinetic experiment enables us to see how the sorption system is

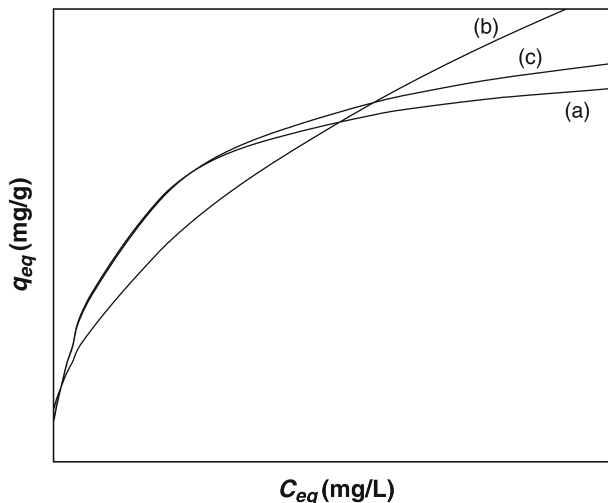

Fig. 12.3. Illustration of the adsorption equilibrium plots (**a**) Langmuir isotherm, (**b**) Freundlich isotherm, and (**c**) Redlich–Peterson isotherm.

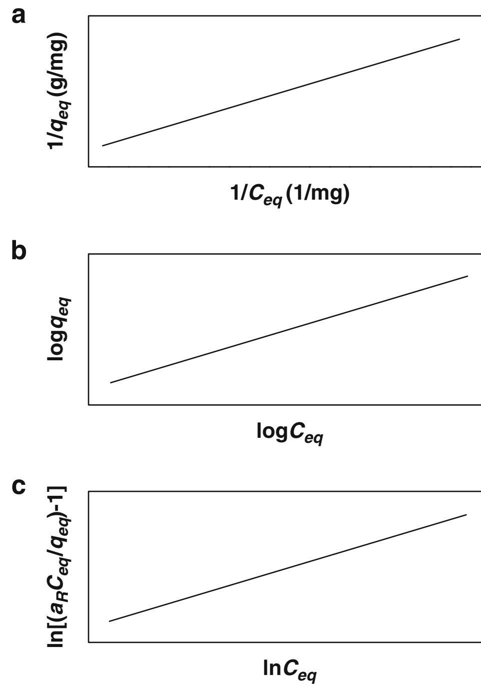

Fig. 12.4. Linearlized equilibrium isotherm equations (**a**) Langmuir isotherm, (**b**) Freundlich isotherm, and (**c**) Redlich–Peterson isotherm.

Table 12.3
Frequently used adsorption isotherm models

Isotherm	Equation	Linearized form	Description
Langmuir	$q_{eq} = q_{max}bC_{eq}/(1 + bC_{eq})$ q_{max}: maximum metal sorption b: affinity	$1/q_{eq} = (1/q_{max}bC_{eq}) + (1/q_{max})$	Monolayer surface adsorption system
Freundlich	$q_{eq} = K_F C_{eq}^{1/n}$ K_F: adsorption capacity n: intensity of heterogeneity	$\log q_{eq} = (1/n) \log C_{eq} + \log K_F$	Heterogeneous surface adsorption system
Redlich–Peterson	$q_{eq} = K_R C_{eq}/(1 + a_R C_{eq}^{\beta})$ β: heterogeneity factor	$\ln[(a_R C_{eq}/q_{eq}) - 1] = \ln K_R + \beta \ln C_{eq}$	Heterogeneous surface adsorption system

affected by process variables and to understand the steps which limit sorption. In addition, the kinetics describes the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid–solution interface. Therefore, it is important to be able to predict the rate at which sorbate is removed from aqueous solutions in order to design appropriate sorption treatment processes. The sorption kinetics, thus, constitute a major criterion in the determination of the interest of sorption processes.

Numerous sorption kinetics have been studied in order to investigate the adsorption phenomena. These kinetic models included the pseudo-first-order kinetic model, the pseudo-second-order kinetic model, and the Elovich kinetic model.

5.1. Pseudo-First-Order Kinetic Model

The Lagergren rate equation (64) was the first rate equation for the sorption of liquid/solid system based on solid capacity. The Lagergren rate equation is one of the most widely used sorption rate equations for the sorption of a solute from a liquid solution. It may be represented as

$$\mathrm{d}q \,/\, \mathrm{d}t = k_1(q_{\mathrm{eq}} - q_t). \tag{7}$$

Integrating Eq. (7) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\log(q_{\mathrm{eq}} \,/\, (q_{\mathrm{eq}} - q_t)) = k_1 t \,/\, 2.303 \tag{8}$$

which is the integrated rate law for a pseudo-first-order reaction, where q_{eq} is the amount of metal sorbed at equilibrium (mg/g); q_t is the amount of metal sorbed at time t (mg/g); and k is the equilibrium rate constant of pseudofirst sorption (1/min). Equation (8) can be rearranged to obtain a linear form

$$\log(q_{\mathrm{eq}} - q_t) = \log q_{\mathrm{eq}} - (k_1 t \,/\, 2.303). \tag{9}$$

The equation applicable to experimental results generally differs from a true first-order equation in two ways (65).

1. The parameter $k_1(q_{\mathrm{eq}} - q_t)$ does not represent the number of available sites.
2. The parameter $\log(q_{\mathrm{eq}})$ is an adjustable parameter. Often it is found not equal to the intercept of a plot of $\log(q_{\mathrm{eq}} - q_t)$ against t, whereas in a true first order process, $\log(q_{\mathrm{eq}})$ should be equal to the intercept of a plot of $\log(q_{\mathrm{eq}} - q_t)$ against t.

In order to fit Eq. (9) to experimental data, the equilibrium sorption capacity, q_{eq}, must be known. In most cases in the literature, the pseudo-first-order equation of Lagergren does not fit well for the whole range of contact time. In Eq. (9), one has to find some means of extrapolating the experimental data to $t = 1$, or treat q_{eq} as an adjustable parameter to be determined by trial and error. For this reason, it is necessary to use a trial and error method to obtain the equilibrium sorption capacity, q_{eq}.

5.2. Pseudo-Second-Order Kinetic Model

If the sorption rate of system is a pseudo-second-order mechanism, the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or the exchange of electrons between sorbent and sorbate as covalent forces. There are certain assumptions in description of this kinetic model (66).

1. There is a monolayer of metal ion on the surface of sorbent
2. The energy of sorption for each ion is the same and independent of surface coverage
3. The sorption occurs only on localized sites and involves no interactions between sorbed ions
4. The rate of sorption is almost negligible in comparison with the initial rate of sorption

The kinetic rate equation can be written as follows:

$$dq_t \,/\, dt = k_2(q_{eq} - q_t)^2, \tag{10}$$

where k is the rate constant of sorption, (g/mg min), q_{eq} is the amount of divalent metal ion sorbed at equilibrium, (mg/g), q_t is amount of divalent metal ion on the surface of the sorbent at any time, t, (mg/g).

Separating the variables in Eq. (10) gives:

$$dq_t \,/\, (q_{eq} - q_t)^2 = k dt. \tag{11}$$

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$; the integrated form of Eq. (11) becomes:

$$1 \,/\, (q_{eq} - q_t) = 1 \,/\, q_{eq} + kt \tag{12}$$

which is the integrated rate law for a pseudo-second-order reaction.

Equation (12) can be rearranged to obtain:

$$q_t = t \,/\, \left(1 \,/\, kq_{eq}^2 + t \,/\, q_{eq}\right) \tag{13}$$

which has a linear form of

$$t/q_t = 1 \,/\, \left(k_2 q_{eq}^2\right) + (1 \,/\, q_{eq})t. \tag{14}$$

If the initial sorption rate is

$$h = kq_{eq}^2, \tag{15}$$

then Eqs. (13) and (14) become:

$$q_t = t \,/\, (1 \,/\, h + t \,/\, q_{eq}) \tag{16}$$

and

$$t \,/\, q_{eq} = 1 \,/\, h + t \,/\, q_{eq}. \tag{17}$$

The constants can be determined experimentally by plotting of t/q_t against t.

5.3. Elovich Kinetic Model

A widely used equation to describe the kinetics of chemisorption is the Elovich equation

$$dq \,/\, dt = a \exp(-\mathrm{b}q_t), \tag{18}$$

where a and b are parameters of the equation. The parameter a is regarded as the initial rate because $dq/dt \to a$ as $q \to 0$ and parameter b is related to the extent of surface coverage and activation energy for chemisorption.

Given that $q = 0$ at $t = 0$, the integrated form of Eq. (18) becomes:

$$q_t = (1 \,/\, b) \ln(t + t_0) - (1 \,/\, b) \ln t_0, \tag{19}$$

where $t_0 = 1/ab$. If $t \gg t_0$, Eq. (19) is simplified as:

$$q_t = (1\,/\,b)\ln(ab) + (1\,/\,b)\ln t. \tag{20}$$

The application of the Elovich equation in liquid phase sorption is gaining in popularity. The Elovich equation was also successfully used to describe the sorption kinetics of ion-exchange system (8).

The three kinetic models are summarized in Table 12.4 and Fig. 12.5.

Table 12.4
Frequently used sorption kinetic models

Kinetic model	Equation	Linearized form	Description
Pseudo-first-order	$dq/dt = k_1(q_{eq} - q_t)$	$\log(q_{eq} - q_t) = \log q_{eq} - (k_1 t/2.303)$	Trial and error method was required to obtain q_{eq} value
Pseudosecond order	$dq_t/dt = k_2(q_{eq} - q_t)^2$	$t/q_t = 1/(k_2 q_{eq}^2) + (1/q_{eq})t$ $t/q_{eq} = 1/h + t/q_{eq}$ $h = kq_{eq}^2$: initial rate	It must be assumed that the sorption follows the Langmuir equation
Elovich	$dq/dt = a\exp(-bq_t)$	$q_t = (1/b)\ln(ab) + (1/b)\ln t$ A: initial rate B: extent of surface coverage	Successfully used to describe the chemisorption kinetics

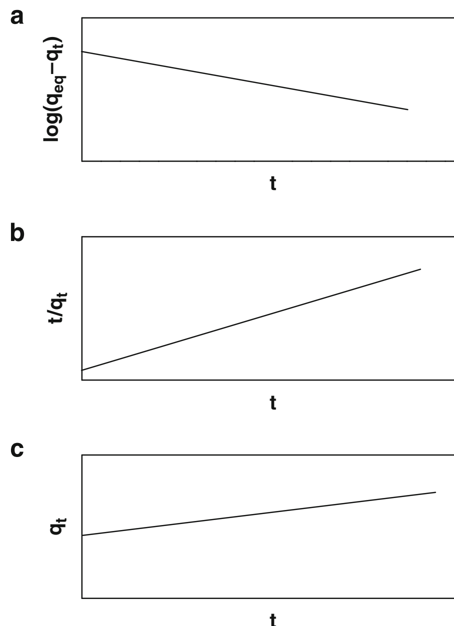

Fig. 12.5. Linearlized kinetic model equations (**a**) pseudo-first-order kinetic, (**b**) pseudo-second-order kinetic, and (**c**) Elovich kinetic.

6. EXAMPLES

Example 1

The biosorption experiment was done using 250-mL Erlenmeyer flask with 50 mL of metal-bearing solution of initial metal concentration of 100 mg/L. The quantity of used biomass was 0.1 g and final equilibrium concentration of metal was 25 mg/L after allowing enough time for developing the sorption equilibrium. Calculate the specific sorption value (mg/g).

Solution

The specific metal sorption value was calculated using the following equation:

$$q_{eq} = V(C_i - C_{eq})/1{,}000M,$$

where q is the specific metal sorption (mg metal/g of biomass), V is the volume of metal solution (mL), C_i and C_{eq} are the initial and equilibrium concentration of metal (mg metal/L) respectively, M is the dry weight of the biomass (g).

Thus, $q_{eq} = 50(100 - 25)/1{,}000 \times 0.1 = 37.5$

Therefore, the specific metal sorption value is 37.5 (mg metal/g of biomass).

Example 2

The M^{2+} biosorption experiments by biomass A were done under different initial metal concentrations. 0.1 g of biomass was added to 50 mL of solution of M^{2+} in 250-mL Erlenmeyer flasks shaken at fixed rpm in an orbital shaker at constant temperature for enough time to obtain equilibrium. The results obtained at different initial metal concentrations are shown in Table 12.5.

(a) Draw the linear plot of Langmuir isotherm for biosorption of M^{2+} by biomass A.
(b) Draw the linear plot of Freundlich isotherm for biosorption of M^{2+} by biomass A.
(c) Find the Langmuir and Freundlich isotherm parameters and correlation coefficient of each isotherm for biosorption of M^{2+} by biomass A.
(d) Determine the more suitable isotherm model to explain this biosorption system. Explain the meaning of this result.

Solution

(a) To draw the linealized equation of Langmuir isotherm, the parameters of Eq. (2) can be calculated from Table 12.5 and shown in Table 12.6. The linear plot of Langmuir isotherm can then be drawn in Fig. 12.6.
(b) To draw the linealized equation of Freundlich isotherm, the parameters of Eq. (4) can be calculated from Table 12.5 and shown in Table 12.7. The linear plot of Freundlich isotherm can then be drawn in Fig. 12.7.
(c) The calculated isotherm parameters are presented in Table 12.8.
(d) The Langmuir isotherm gives a good fit for all experimental data than Freundlich isotherm. Conformity of these data to the Langmuir model indicated that this biosorption system could be characterized as a monolayer, single site type phenomenon with no interaction between ions adsorbed in neighboring sites.

Table 12.5
The results obtained at different initial metal concentrations

Initial M^{2+} concentration (mg/L), C_i	Equilibrium M^{2+} concentration (mg/L), C_{eq}
20	5.6
25	7.4
30	9.4
50	16.6
70	22.7
100	34.5
200	98.9
300	180.5
400	279.7
500	375.1
600	470.0

Table 12.6
The equation parameters of Langmuir isotherm for linear plot

Initial M^{2+} concentration (mg/L), C_i	Equilibrium M^{2+} Concentration (mg/L), C_{eq}	q_{eq} (mg/g)	$1/q_{eq}$ (g/mg)	$1/C_{eq}$ (1/mg)
20	5.6	7.22	0.139	0.180
25	7.4	8.79	0.114	0.135
30	9.4	10.30	0.097	0.106
50	16.6	16.70	0.060	0.060
70	22.7	23.65	0.042	0.044
100	34.5	32.75	0.029	0.030
200	98.9	50.55	0.010	0.010
300	180.5	59.75	0.006	0.006
400	279.7	60.17	0.004	0.004
500	375.1	62.50	0.003	0.003
600	470.0	65.00	0.002	0.002

Example 3

The biosorption of M^{2+} by biomass B were carried out under initial metal concentrations of 50, 100, 200, and 300 mg/L. 0.1 g of biomass was added to 50 mL of solution of M^{2+} in 250-mL Erlenmeyer flasks shaken at fixed rpm in an orbital shaker at constant temperature. The q_{eq} values with time at different initial metal concentrations are shown in Table 12.9. If the rate of sorption of M^{2+}biosorption by biomass B is pseudo-second-order kinetic, find the second-order rate constants for this biosorption system.

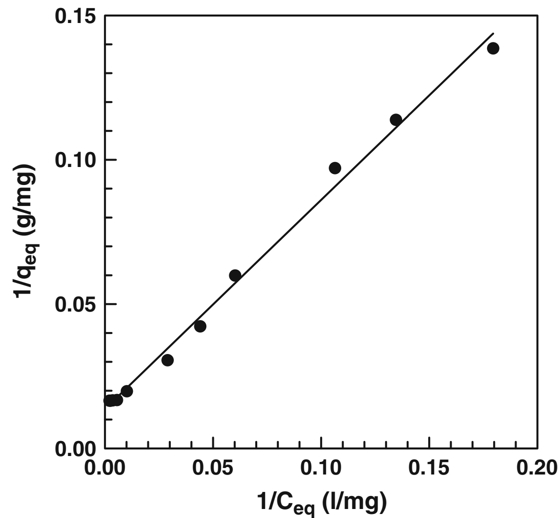

Fig. 12.6. Linear plot of Langmuir isotherm.

Table 12.7
The equation parameters of Freundlich isotherm for linear plot

Initial M^{2+} concentration (mg/L), C_i	Equilibrium M^{2+} concentration (mg/L), C_{eq}	q_{eq} (mg/g)	log q_{eq}	log C_{eq}
20	5.6	7.22	0.858	0.746
25	7.4	8.79	0.944	0.871
30	9.4	10.30	1.013	0.973
50	16.6	16.70	1.223	1.220
70	22.7	23.65	1.374	1.356
100	34.5	32.75	1.515	1.538
200	98.9	50.55	1.704	1.995
300	180.5	59.75	1.776	2.256
400	279.7	60.17	1.779	2.447
500	375.1	62.50	1.795	2.574
600	470.0	65.00	1.813	2.672

Solution

The second-order rate constants can be determined by plotting of t/q_t against t from Eq. (14). The plot of t/q_t against t is shown in Fig. 12.8.

The slopes and intercepts of the straight line from Fig. 12.8 and second-order rate constants determined from this data are shown in Table 12.10. The slopes and intercepts of Fig. 12.8 are $1/q_{eq}$ and $1/(k_2 q_{eq}^2)$ in Eq. (14), respectively.

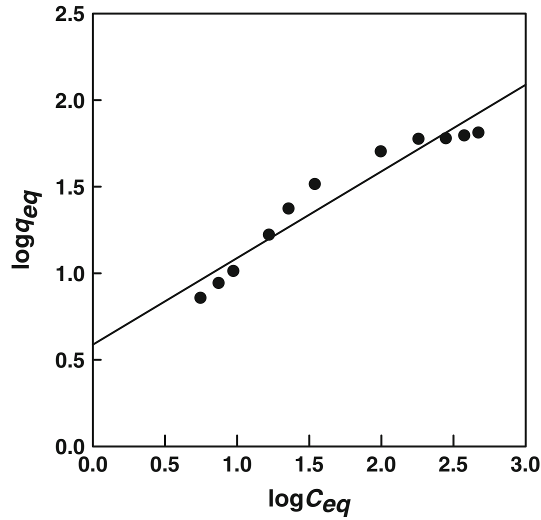

Fig. 12.7. Linear plot of Freundlich isotherm.

Table 12.8
Langmuir and Freundlich isotherm parameters

Isotherm model	Parameters	Value	R^2
Langmuir	$q_{\max}$ (mg/g)	73.5	0.994
	b (1/mg)	0.02	
Freudlich	K_F	3.9	0.931
	N	2.0	

Table 12.9
The q_{eq} values with time at different initial metal concentrations

t (min)	C_i (mg/L)			
	50	100	200	300
	q_t (mg/g)			
1	16.1	25.1	27.0	28.9
5	16.9	26.8	28.0	30.0
10	17.2	28.6	30.5	31.6
30	17.8	29.1	32.2	33.4
60	18.5	30.9	33.9	35.6
90	19.0	31.1	34.1	36.2
120	19.4	31.9	34.3	36.5
150	19.3	31.9	35.0	36.8
180	19.3	31.9	35.0	36.9

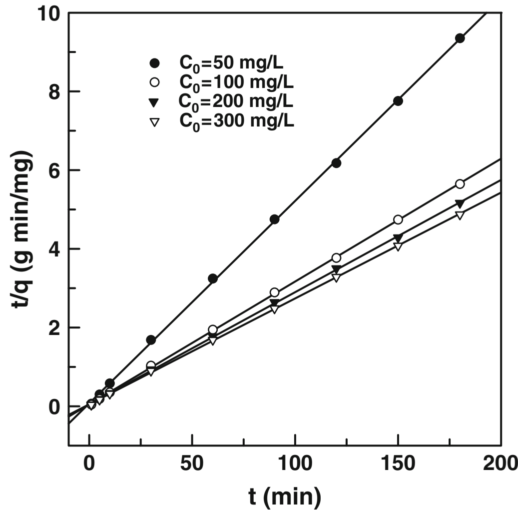

Fig. 12.8. The plot of t/q_t against t.

Table 12.10
The slope and intercept of the straight line from Fig. 12.8 and second order rate constants determined from this data

C_i (mg/L)	Slope	Intercept	$k_2 \times 10^2$ (g/mg min)	R^2
50	0.0514	0.0737	3.58	0.999
100	0.0312	0.0471	2.07	0.999
200	0.0285	0.0468	1.74	0.999
300	0.0269	0.0487	1.49	0.999

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