Chapter 7
Bio-based Methods for Wastewater Treatment: Green Sorbents

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7.1 Introduction

The global environment is under great stress due to urbanization and industrialization as well as population pressure on the limited natural resources [1]. The availability of water resources is becoming increasingly scarce; the consumption and exploitation of water resources, along with an exponential increase in population have caused water pollution [2–4]. About 80 % of the world's population lives in areas with high water security threats, the most severe category encompassing 3.4 billion people, almost all in developing countries [5]. One of the Millennium Development Goals (MDGs) is to halve, by 2015, the proportion of people that did not have access sustainable sanitation. In 2002, 1.1 billion people did not have access to a reliable water supply and 2.6 billion people lacked access to adequate sanitation [6]. Moreover, the needs of water for agriculture, industry, and domestic have steadily increased. These withdrawals are projected to continue increasing, placing further pressure on aquatic ecosystems [5]. Regarding Fig. 7.1, United States Environmental Protection Agency (USEPA) stated that heavy metals are the most contaminants in industrial effluents [7].

Most of the pollutants and heavy metals discharged in industrial effluents ultimately find their way to aquatic ecosystems. Metals are omnipresent constituents in the biosphere, vital to our industry, infrastructure, and daily life. Since the industrial revolution, metals have increasingly been redistributed in the environment, with accumulation in terrestrial and aquatic habitats being associated with adverse effects on the biota and human health [8]. Heavy metals are elements having atomic weights between 63.5 and 200.6, and specific gravity greater than 5.0 [9]. Heavy metals are

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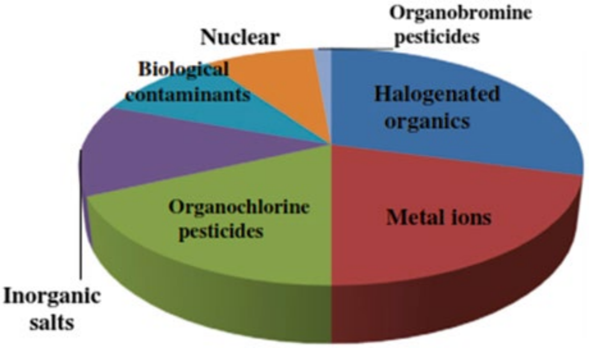

Fig. 7.1 Distribution of contaminants regulated by United States Environmental Protection Agency (USEPA) (Reproduced from [7])

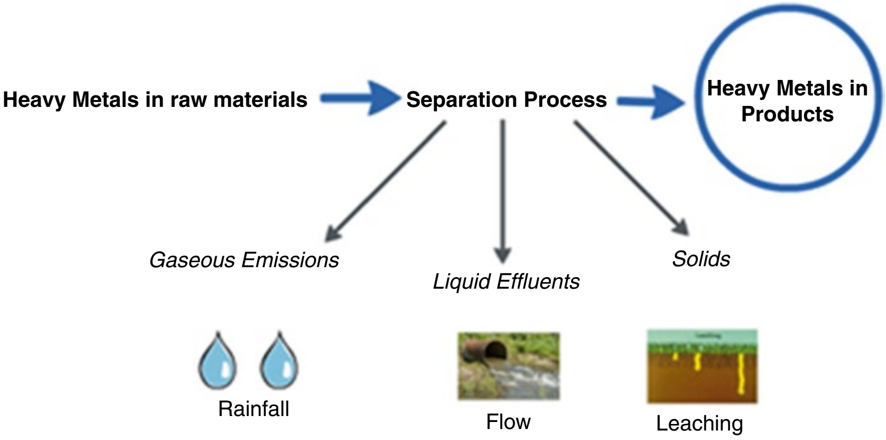

Fig. 7.2 Heavy metals sources in water bodies

the main group of inorganic contaminants, and a considerable large area of land is contaminated with them due to use of sludge, pesticides, fertilizers, and emissions from municipal waste incinerators, car exhausts, and smelting industries [10]. For example, heavy metals can be existed into water during rainfall, and they are leached from solids into surface streams and rivers. Moreover, effluents from industries are often discharged directly into rivers or other receiving surface water bodies [11] as shown in Fig. 7.2.

Toxic heavy metals of particular concern in treatment of industrial wastewaters include: mercury, lead, cadmium, zinc, copper, nickel, and chromium [9, 12] and the metals that defined as priory pollutants are: Pb, Cr, Hg, Se, Zn, As, Cd, Au, Ag, Cu, and Ni [13]. Various methods exist for the removal of heavy metal ions from wastewater which include chemical precipitation, ion exchange, reverse osmosis, solvent extraction, and adsorption. The traditional adsorbent material was Activated Carbon (AC). However, the use of (AC) is restricted due to high cost and its adsorption capacity gets lower after regeneration process in comparison with the virgin-activated carbon [14].

Among all the treatment processes mentioned, phytoremediation is one new cleanup concept that involves the use of plants to clean contaminated water [15]. It includes two uptake processes: an initial fast, reversible, metal-binding process (biosorption); and a slow, irreversible, ion sequestration step, bioaccumulation [16]. As a specific term, biosorption is used to depict a method that utilizes materials of biological origin biosorbents formulated from nonliving biomass for the removal of target substances from aqueous solutions. Biosorption "traditionally" covers sequestration of heavy metals as well as rare earth elements and radionuclides or metalloids, but the research and applications extended to the removal of organics, namely dyes [17]. The "bio" prefix refers to the involvement of biological entity, which is living organisms, dead cells and tissues, cellular components or products. The ultimate goal of these efforts is to provide an economical and eco-friendly technology, efficiently working also at metal levels below 10 mg L^{-1}. These are the features that living as well as dead biomass could be challenged for [18].

The natural capacity of microorganisms, fungi, algae, and plants to take up heavy metal ions and radio nuclides and, in some cases, to promote their conversion to less toxic forms has sparked the interest of (micro) biologists, biotechnologists, and environmental engineers for several decades. Consequently, various concepts for "bio-removal" of metals from waste streams and bioremediations of contaminated environment are being proposed, some of which were brought to pilot or industrial scale [19–23]. There are generally three routes to follow considering "bio-removal" of metallic species from solutions. The first two rely on properties of living cells and involve active metal uptake-bioaccumulation (i.e., plasma membrane mediated transport of metal ion into cellular compartment) and eventual chemical conversion of mobile metal to insoluble forms. The later may occur in the cytoplasm, at the cell surface or in the solution by precipitation of metal ion with metabolites, via redox reactions or by their combination [24]. The effectiveness of the process will depend on the (bio) chemistry of particular metal and on metabolic activity of eligible organism, which is in turn affected by the presence of metal ions. To this point, the use of metallotolerant species or physical separations of the production of metal-precipitating metabolite from metal precipitation in contaminated solution produce viable methods for treatment of industrial effluents [25]. Several of them are to various extents dependent on or involve the metabolism-independent metal uptake event at the cell wall by polysaccharides, associated molecules, and functional groups. This metal sequestration capacity is commonly known as biosorption, which itself represents the third potent way of "bio-removal" of metals from solution [18].

The majority of biosorption studies tested one-factor-at-a-time on the biosorption process. For example, equilibrium and kinetics models [4]. However, few studies examined three or four parameters and their interaction on the biosorption process using the factorial experimental design [16, 26–29]. The choice of such experimental design has two main objectives:

- Minimize bias.
- Minimize the variability of observations, with the aim of obtaining powerful statistical tests and precise estimates.

The aim of this chapter is to provide an overview of wastewater treatment methodologies with special references to phytoremediation. Biosorption mechanism and key factors controlling it are also elucidated.

7.2 Conventional Treatment Methods for Wastewater

There is growing consideration to abandon the conventional water treatment methods because of their high cost and environmental impact. Table 7.1 gives a summary of the pros and cons of some of the used technologies for the wastewater treatment. Each method mentioned in Table 7.1 has its own limitations in industrial applications, for instance, low selectivity, complex to operate, high capital, and energy costs. In addition, it is also inefficient in treating waste streams that contain low concentrations of contaminants and may fail when handling wastes of complex chemistry [30].

Table 7.1 Pros and Cons of conventional treatment methods for wastewater

Conventional treatment methods	Pros	Cons	References
Chemical precipitation	• Low capital cost, simple operation • Effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L	• The demand of a large amount of chemicals • Generates sludges • Generally, it cannot be used to handle low concentration of metal wastewater, which is below 100 mg/L	[31–33]
Ion exchange	• Effective to treat inorganic effluent with a wide metal concentration of less than 10 mg/L to higher than 100 mg/L • No sludge generation • Metal recovery	• Require pretreatment • Suitable ion-exchange resins are not available for all heavy metals • Expensive • Ion-exchange resins must be regenerated by chemical reagents when they are exhausted and the regeneration can cause serious secondary pollution	[9, 31, 32]

(continued)

Table 7.1 (continued)

Conventional treatment methods	Pros	Cons	References
Coagulation–flocculation	• Shorter time to settle out suspended solids	• Sludge production • Extra operational cost for sludge disposal • Generally, coagulation flocculation can't treat the heavy metal wastewater completely. Therefore, coagulation flocculation must be followed by other treatment techniques • Large consumption of chemicals	[9, 34]
Reverse Osmosis	• Purifies water by removing salts such as calcium, magnesium, sodium ion, chloride ion, copper ion, as well as bacteria	• Low recovery • Brine disposal • High maintenance	[35]
Ultrafiltration (UF)	• Potentially applicable in many areas such as high water flux, high water purity, membrane fouling, and high mechanical, chemical, and thermal stability	• Since the pore sizes of UF membranes are larger than dissolved metal ions in the form of hydrated ions, these ions would pass easily through UF membranes	[9, 35]
Microfiltration	• Separates larger size particles such as suspended solids, fixed solids, and microorganisms • The membranes exhibit high porosity and have distinct pores	• Permeates micrometer-sized particles present in water	[36]

7.3 Biosorption Vs. Bioaccumulation

Biosorption is a process with some unique characteristics. It can effectively sequester dissolved metals from very dilute complex solutions with high efficiency. This makes biosorption an ideal candidate for the treatment of high volume low concentration complex wastewaters. It is a physical–chemical process, simply defined as the removal of substances from solution by biological material. This is a property of both living and dead organisms, and has been heralded as a promising biotechnology because of its simplicity, analogous operation to conventional ion-exchange technology, apparent efficiency, and the availability of biomass wastes [37, 38]. On the other hand, bioaccumulation is metabolically active and is performed by living cells [39]. It is the accumulation of contaminant via all routes available to the organism [40]. Biosorption and bioaccumulation differ in that in the first process pollutants are bound to the surface of cell wall; passive and based mainly on the "affinity" between the sorbent and sorbate and in the second, they become also accumulated inside the cell; it is based on active metabolic transport [41]. The comparison between biosorption and bioaccumulation process is illustrated in Table 7.2.

Table 7.2 Comparison between biosorption and bioaccumulation process

Features	Biosorption	Bioaccumulation	References
Process	• Passive process • Adsorption; metals are bound with cellular surface	• Active process • Absorption; metals are bound with cellular surface and interior	[39]
Biomass	Growth independent; not alive (Single-stage)	Alive (Double-stage)	[39]
Rate of uptake	Usually rapid. Most biosorption mechanisms are rapid.	Usually slower than biosorption. Since intracellular accumulation is time-consuming	[41]
Metal affinity	High under favorable conditions	Toxicity will affect metal uptake by living cells, but in some instances high metal accumulation depends on the toxicity of the pollutant	[41]
Storage	Easy to store and use	External metabolic energy is needed for maintenance of the culture	[41]
Versatility	• Metal uptake may be affected by anions or other molecules • Extent of metal uptake usually pH dependent • The binding sites can accommodate a variety of ions	• Requires an energy source; dependent on plasma membrane ATPase activity • Not very flexible. Prone to be affected by metal/salt conditions	[41]
Selectivity	Poor as Variety of ligands involved. However, selectivity can be improved by modification/processing of biomass	Better than biosorption, but less than some chemical technologies	[41]

(continued)

Table 7.2 (continued)

Features	Biosorption	Bioaccumulation	References
pH	The solution pH strongly influences the uptake capacity of biomass However, the process can be operated under a wide range of pH conditions	In addition to uptake, the living cells themselves are strongly affected under extreme pH conditions	[41]
Regeneration and Reuse	High possibility of biosorbent regeneration, with possible reuse over a number of cycles	Since most toxicants are intracellularly accumulated, the chances are very limited	[31]
Cost	Usually low	• Usually high • The process involves living cells and cell maintenance is cost prone	[41]

Previous studies reported that dead biomass or agricultural waste accumulates heavy metal ions greater extent than living cells. As the changes that occur in the cell structure after the cells are dry-killed, affect adsorption in a positive manner [42]. However, [43] studied biosorption of Pb^{2+}, Cd^{2+}, Cu^{2+}, and Ni^{2+} by nonviable and viable granular sludge biomass. The first uptake process is biosorption or passive uptake. It involves the binding of metal ions to the cell surface and the second uptake process is intracellular uptake, active uptake or bio-accumulation. It was found that the efficiency of nonviable cells in biosorbing metal ions may be less than that of the living cells but the use of nonviable biomass offers the following advantages over viable cells:

- Metal removal is not subject to toxicity limitations of living biomass
- No requirements for growth media and nutrients
- Biosorbed metal ions can be easily desorbed and biomass can be reused
- Biomass can be stored for a long period of time
- Biosorption that tends to be rapid

Therefore, nonviable biomass was used to overcome the disadvantages of using viable biomass. Also, the major advantages of biosorption are low cost, high efficiency, minimization of chemical or biological sludge, regeneration of biosorbents, and possible metal recovery. The successful of such biosorption process depends on using suitable biosorbents. Thus, characteristics of a suitable biosorbent for its successful application to industrial scale can be as the following [44]:

- Operation over wide range of pH, temperature, and other physicochemical parameters
- No secondary pollutants released
- Good stability under acidic/alkaline environments
- Good uptake capacity towards different ions

- Cost-effective
- No pretreatment necessity
- Sequential removal of metal ions
- Easy desorption and reuse ability
- No requirement of chemical modification or immobilization
- Easy adaptability to different system designs

7.4 Factors Affecting Biosorption Process

7.4.1 Contact Time

The contact time between adsorbent and adsorbate has a significant role to reach equilibrium in biosorption experiments. Liu et al. [45], Singanan and Peters [46] and Mahmoud et al. [47] concluded that the rate of adsorption is higher at the first hour of the biosorption process due to availability of a large number of active sites on the biosorbents' surface, then it becomes slower in the range of hour to three hours as these sites are exhausted by the rate at which the adsorbate is transported from the exterior to the interior sites of the biosorbents. With this account, the adsorption capacity or removal percentage did not vary significantly as a general for most heavy metals after 3 h.

7.4.2 Agitation Rate

Agitation rate is also an important factor in biosorption process because mass transfer resistance can minimize the uptake of metal ions from the aqueous solutions. The boundary layer resistance could be affected by the rate of agitation [48]. When increasing the agitation rate, the diffusion rate of a solute from the bulk liquid to the liquid boundary layer surrounding particles becomes higher due to the enhanced turbulence and the decrease in the thickness of the liquid boundary layer. Wong et al. [49] found that the uptake of Pb^{2+} and Cu^{2+} increased with increasing agitation rate and the maximum uptake was at 250 rpm.

7.4.3 Metal Ion Concentration

The removal percentages of most heavy metals were decreased with increasing the concentration of these metals. This is because the biomass surface area available for metal biosorption at low metal ion concentration was higher. Moreover, the ability of active sites to fully absorb the metal ions at lower concentrations is meant that the ratio of active adsorption sites to the initial metal ions is larger, resulting in higher removal efficiency. After that, with increasing metal ion concentration, the functional groups on biomass surface could be saturated, and there were a few available active sites on the biomass surface so the metal ions are competed for the available binding sites [50–52]. This is in line with previous studies done by Amarasinghe and Williams [53], Abdel-Aty et al. [54] and Mahmoud et al. [47].

7.4.4 pH of the Aqueous Solution

It is one of the important factors that significantly influence metal sorption [4, 55]. At lower pH values, the H_3O^+ ions compete with the metal ions for the exchange sites in the sorbent [56]. Arief et al. [57] explained this finding by the fact that when the concentration of H^+ ions was high, Cd^{2+} ions must compete with H^+ ions in order to attach to the surface functional groups of the agricultural wastes. Also, they found that when the pH value rise, fewer H^+ ions exist, and consequently, Cd^{2+} ions have a better chance to bind at free binding sites. As pH increased, the negative charge density on the adsorbent surface increases due to deprotonation of the metal-binding sites [58]. Similar comments were made by Anirudhan and Sreekumari [59]. They concluded that the increase in metal removal with an increase in pH can be explained on the basis of a decrease in competition between proton and the metal cations for the same functional groups and by the decrease in positive charge of the adsorbent which results in a lower electrostatic repulsion between the metal cations and the surface.

7.4.5 Biomass Dose

It strongly influences the biosorption process because the number of binding sites available for adsorption on the biosorbents is determined by biomass dose in the aqueous solutions [60]. Low biosorbent dose yielded lower percentage removal efficiencies because all biosorbents had a limited number of active sites, which would have become saturated above a certain metal concentration [61]. An increase in the biomass dose generally increased the amount of solute biosorbed, due to the increased surface area of the biosorbent, which in turn increases the number of binding sites [62].

7.4.6 Types of Biomass

A considerable number of bacteria, fungi, algae and yeasts, and different wastes and by-products of the agriculture and food industry have been investigated for their biosorbent metal properties [38]. Indeed, the choice of the biosorbent should consider both efficiency and economy. The efficiency of the process will depend on the biomass chemical composition which varies significantly for different species within the same genus or order [63].

7.4.6.1 Bacterial Surface Display of Metal-Binding Sites

Bacterial surface display has been proved a viable approach for a wide range of medical, industrial and environmental applications. Metal binding by biomolecules of structural components or excreted polymers of bacteria is generally fortuitous and relative efficiencies depend on attributes of the metal ion as well as on reactivity of provided ligands [18]. Shi et al. [64] investigated the efficiency of *Pannonibacter phragmitetus* on the reduction of Cr (VI) from aqueous solution. The maximum rate of Cr removal was found to be 562.8 mg L^{-1} h^{-1}. Miranda et al. [65] have been isolated two species of cyanobacteria, *Oscillatoria laetevirens* and *Oscillatoria trichoides* from a polluted environment and studied for their Cr (VI) removal efficiency from aqueous solutions, the highest removal through biosorption for living biomass was achieved between pH5 and 5.9 and for dead biomass at pH2. Of the two species, living cells of *O. trichoides* were most effective for which removal was 38.7 mg g^{-1} and reached 51.6 % of the total Cr (VI) at 30 mg L^{-1} at pH5–5.9.

Biosorption of hexavalent chromium using biofilm of *Escherichia coli* ASU 7 supported on granulated activated carbon (GAC), lyophilized cells of *Escherichia coli* ASU 7 and granulated activated carbon has been investigated by Gabr et al. [66]. The maximum adsorption removal ($q_{\max}$) of hexavalent chromium calculated from Langmuir equation for biosorption by biofilm, GAC, and bacteria are 97.7, 90.7, and 64.36 mg/g, respectively. The results demonstrate that biofilm supported on GAC, which prepared by impregnation method could be used as promising biosorbent for the removal of Cr (VI) ions from aqueous solutions.

7.4.6.2 Fungal Biosorption and Biosorbents

The common filamentous fungi can sorb heavy metals from aqueous solutions. Fungal biosorption largely depends on parameters such as pH, metal ion and biomass concentration, physical or chemical pretreatment of biomass, presence of various ligands in solution, and to a limited extent on temperature. The cell wall fraction of biomass plays an important role in the sorption of heavy metals [18]. Trivedi and Patel [67] studied the biosorption efficiency of tropical white-rot basidiomycete on chromium (VI) removal from aqueous solutions. It was found that the pretreatment of fungal biomass with acid resulted in 100 % metal adsorption compared to only 26.64 % adsorption without any pretreatment. Aksu and Balibek [68] studied the biosorption of chromium (VI) from saline solutions on dried *Rhizopus arrhizus* the results showed that the maximum chromium (VI) sorption capacity was for 78.0 mg/g of sorbent.

Srinivasan and Viraraghavan [69] have used two fungal biomasses of *Mucor rouxii* and *Absidia coerulea* along with chitosan and walnut shell media for the removal of oil from water. Moreover, it was found that Nonviable *M.rouxii* biomass is more effective than *A. coerulea* biomass in removing oil from water. The adsorption capacities for standard mineral oil, vegetable oil, and cutting oil were 77.2, 92.5, and 84 mg/g of biomass, respectively. However, these capacities using *M. rouxii* biomass were less than those obtained with chitosan and walnut shell media.

7.4.6.3 Plants and Agricultural Wastes as Biosorbents

Biosorption onto plants and raw agricultural waste is a low-cost treatment technique for the removal of contaminants, including heavy metals, from water and wastewater. Aoyama et al. [70] studied the biosorption of Cr (VI) from wastewater on using Japanese cedar Cryptomeria japonica bark. Igwe and Abia [71] investigated the biosorption efficiency of some agricultural wastes as maize husk on the removal of Cd(II), Pb(II), and Zn(II) ions from aqueous solutions. It was found that the modification of the biosorbent by EDTA enhanced the biosorption capacity. Jain et al. [72] studied the biosorbent efficiency of sunflower *Helianthus annuus* waste for Cr (VI) removal from wastewater under different experimental conditions and biosorbent treatments, either in boiling water or in formaldehyde. Obtained efficiencies were 81.7 and 76.5 % for boiled and formaldehyde treated biosorbent, respectively (4.0 g/L) biosorbent dose.

Zein et al. [73] investigated the biosorption efficiency of mangosteen shell, Garcinia mangostana shell for the removal of Pb(II), Cd(II), and Co(II). The sorption capacity of Pb(II), Cd(II), and Co(II) reached 3.56 mg/g, 3.15 mg/g, and 0.34 mg/g, respectively. García-Rosales and Colín-Cruz [74] investigated the efficiency of Maize (Zea mays) stalk sponge as a biosorbent for lead in aqueous solutions, it was found that Zea mays biosorbent is effective in reducing Pb(II) concentrations in industrial wastewater. Ibrahima et al. [75] suggested the use of an abundantly available agricultural waste modified soda lignin from oil palm empty fruit bunches, for the removal of lead (II) ions from aqueous solution. Tan et al. [76] has the biosorption efficiency of dried *Azolla filiculoides* on the removal of Basic Organic (BO) as a target pollutant from aqueous solution. The obtained results showed that the removal ratio of BO from wastewater containing 100 mg/L BO reached 79.3 %. Thus, this high biosorption capacity indicates the high efficiency of *Azolla filiculoides* biomass for the removal of BO from industrial wastewater.

Carro et al. [77] studied the biosorption capacity of *Pteridium aquilinum* for the removal of mercury from aqueous solution. It was found this sorption process takes place via neutral species and almost 100 % of mercury was sorbed at pH values above 5. Ashraf et al. [78] have investigated the biosorption capacity of *Mangifera indica* on the removal of Pb(II), Cu(II), Zn(II), and Ni(II) ions from aqueous solution. The percent removal of these metal ions reached 82.76 % for lead, 76.60 % for copper, 63.35 % for zinc, and 59.35 % for nickel. Lü et al. [79] tested the biosorption efficiency of lawny grass for the removal of Cd (II) from aqueous solution the biosorption capacity of Cd(II) reaches its maximum at 145(mg/g), thus revealing the efficient performance of lawny grass on metal ions removal.

The biosorption of Cd (II) from aqueous solution using *Ananas comosus* (AC) peel, *Parkia speciosa* (PS) pods and *Psidium guajava* (PG) peel was evaluated by Foo et al. [80]. It was found that the adsorption capacities reached 18.21 mg/g (AC peel), 25.64 mg/g (PS pods), and 39.68 mg/g (PG peel). Jeon [81] studied the biosorption efficiency of Rice hulls on the removal of copper ions from aqueous solution. It was found that the maximum removal capacity of copper ions was 11.83 mg/g.

Thus, rice hulls could be sufficiently used as a promising biosorbent in the copper ion removal process. Ding et al. [82] studied the biosorption efficiency of tea waste on the removal and the recovery of U (VI) from the aqueous solution. The removal and recovery percentages were up to 86 % and 80 %, respectively. Moreover, it was found that the biosorption of U(VI) by tea waste is a physical multilayer adsorption.

The capability of durian shell waste biomass as a novel and potential biosorbent for Cr (VI) removal from aqueous solution has been investigated by Kurniawan et al. [83] the maximum biosorption capacity of durian shell was 117 mg/g. Shukla and Vankar [84] studied the adsorption efficiency of Araucaria leaves on the removal of Cr (VI) ions from aqueous solution. The biosorption efficiency observed was maximum 100 %. Khoramzadeh et al. [85] have investigated the biosorption efficiency of Sugarcane Bagasse for Mercury removal from aqueous solutions. Moreover, Mahmoud et al (Mahmoud, A.E.D. and M. Fawzy, Statistical Methodology for Cadmium (Cd(II)) Removal from Wastewater by Different Plant Biomasses. Journal of Bioremediation & Biodegradation, 2015) studied the behavior of two different plant biomasses; rice straw (*Oryza sativa*) and dragon tree leaves (Dracaena draca) on the cadmium biosorption.

7.5 Biosorption Isotherms

Biosorption isotherm is a graphical representation expressing the relation between the mass of sorbed metal at constant temperature per unit mass of biosorbent q_e (mg/g) solid phase concentration of the sorbate and liquid phase metal concentration at equilibrium (Ce). It illustrates the metal distribution between the liquid and solid phases at various equilibrium concentrations, thus providing information concerning the biosorption mechanism and revealing how efficiently a given biosorbent interacts with the sorbate. Also, it is used as indication to estimate the economic feasibility of biosorbent for specific commercial applications [86, 87]. Biosorption isotherms can be generated based on theoretical principles. Three biosorption isotherm models have been tested in this study, namely, Langmuir, Freundlich, and Temkin, in order to describe the equilibrium characteristics of adsorption.

7.5.1 Langmuir Isotherm

Langmuir isotherm is an analytical equation basically developed for gas phase adsorption onto the homogeneous glass and metal surfaces [18, 88]. The assumptions of the Langmuir isotherm are:

(a) Adsorption energy is constant on all sites (all sorption sites are uniform)
(b) Adsorbed atoms or molecules are adsorbed at definite, localized sites
(c) Each site can accommodate only one molecule or atom (only one sorbate)
(d) There is no interaction between sorbed species
(e) One sorbate molecule reacts with only one active site

7.5.2 *Freundlich Isotherm*

Freundlich isotherm is applicable to both monolayer and multilayer adsorption, and it is based on made two assumptions which are first, heterogeneous surface energies that is, exponential variation in site energies second, surface adsorption is not the rate-limiting step [89, 90].

7.5.3 *Temkin Isotherm*

Temkin isotherm assumes that the heat of sorption or adsorption decreases linearly with the surface coverage, that is the energy of adsorption decreases as the degree of completion of the sorptional centers of biosorbent increases. This is mainly due to the adsorbent–adsorbate interactions [91, 92].

7.6 Biosorption Kinetics

Biosorption kinetic studies are essential to select the optimum conditions for full-scale batch process. The kinetic parameters, which are helpful for the prediction of biosorption rate, provide significant information for designing and modeling the biosorption process. Biosorption kinetics was analyzed based on the pseudo first-order and the pseudo second-order kinetic models to find the optimum biosorption kinetic constants [88, 93].

7.6.1 *Pseudo First-Order Equation*

The adsorption models were first described by the Lagergren pseudo first-order model [90, 93] that illustrates the sorption rate based on the sorption capacity. It is the ideal model of sorption, 1:1; (i.e.,) one sorbate molecule occupies one activated site.

7.6.2 *Pseudo Second-Order Equation*

The sorption kinetics was described by the pseudo second-order model [94]. It has been applied for the analysis of the kinetics of chemisorption processes. However, it relies on the assumption that the rate of occupation of sorption sites is proportional to the squares of the unoccupied sites. In other words, it assumes that an adsorbate molecule is adsorbed on two sorption sites; thus, two molecules to one active site [95]. Aoyama and Kishino [70] investigated the biosorption of Cr (VI) from aqueous solution on japanese cedar (*Cryptomeria japonica*) bark. The obtained results at different temperatures obeyed Langmuir adsorption isotherm.

Aksu and Balibek [68] investigated the biosorption efficiency of dried *Rhizopus arrhizus* and in salt-containing medium on the removal of chromium (VI) from aqueous solution. Experimental data fitted Langmuir–Freundlich sorption model. Sorption capacity of dried *R. arrhizus* used in this study is q_e 114.9 mg/g. Pseudo first-order, pseudo second-order, and saturation type kinetic models described the biosorption kinetics accurately at all chromium (VI) concentrations in the absence and in the presence of changing concentrations of salt all theoretical data obtained from kinetic models were in good agreement with the experimental results.

Elangovan et al. [96] investigated the removal of Cr(VI) and Cr(III) from aqueous phase using different aquatic weeds. The adsorption process for all biosorbents was a second-order process. The maximum sorption capacity for Cr(III) achieved using reed mat was 7.18 mg/g. However, in case of Cr(VI), mangrove leaves were the best for its removal (8.87 mg/g), followed by water lily (8.44 mg/g). Thus, aquatic weeds seem to be a promising biosorbent for the removal of chromium ions from water environment.

Gokhale et al. [97] studied the biosorption of immobilized *Spirulina platensis* on the removal of chromium (VI) from aqueous solution. The percent adsorption was 99 % from an aqueous solution containing 100 mg/L chromium (VI). Experimental data fitted the Freundlich adsorption isotherm. Gupta and Rastogi [98] investigated the biosorption efficiency of raw and acid-treated *Oedogonium hatei* for the removal of hexavalent chromium from aqueous solutions. Experimental data fitted both Langmuir and Freundlich isotherm models. The biosorption capacities of the raw and acid-treated algae were 31 and 35.2 mg Cr (VI) per g of dry biosorbent, respectively. The pseudo first-order kinetic model adequately describes the kinetic data in comparison to second-order model, and the process involving rate-controlling step is much complex involving both boundary layer and intra-particle diffusion processes.

Gabr et al. [66] investigated the biosorption of Escherichia coli supported on granulated activated carbon for the removal of Cr(VI) from aqueous solution. The biosorption equilibrium data fitted well to both Langmuir and Freundlich. Ibrahim et al. [75] investigated the biosorption capacity of modified soda lignin from oil palm on the removal of lead (II) from aqueous solutions experimental data fitted Langmuir isotherm equation, confirming the monolayer adsorption of lead (II) ions with a biosorption capacity of 46.72 mg/g at 47 °C. The biosorption followed the pseudo second-order equation. Biosorption of arsenic from aqueous solution by algae (*Maugeotia genuflexa*) biomass fitted Freundlich and Dubinin–Radushkevich (D–R) isotherm models. From the Langmuir model, the maximum monolayer biosorption capacity of the biosorbent was found to be 57.48 mg/g at pH6. Kinetic results indicated that the pseudo second-order kinetic model was well fitted to the experimental data [99].

Chen et al. [100] used *Phanero chaetechrysosporium* as a biosorbent for Cr(VI), the maximum removal for Cr(VI) was 344.8 mg/g as determined from the Langmuir isotherm. It was found that pseudo first-order Lagergren models best fitted the data than pseudo second-order Lagergren model. Kurniawan et al. [83] investigated the biosorption capacity of durian shell for the removal of Cr(VI) from synthetic wastewater. Experimental data obeyed Langmuir and Freundlich isotherm models ($R^2 > 0.99$). Also, the pseudo first order prevails over the pseudo second-order model. However, the maximum biosorption capacity of durian shell was 117 mg/g.

7.7 Modeling of Biosorption

Assessment of a solid–liquid sorption system is usually based on two types of investigations: equilibrium models (describe the sorption capacity as a function of chemistry) and kinetics models (describe the sorption history). Recent publications are focused on designing factorial experiments to yield the most relevant response from the wastewater experiments. The process of biosorption involves a solid phase (sorbent) and a liquid phase (solvent) containing a dissolved species (sorbate; metal ions) to be sorbed [63, 101]. The quality of sorbent material is judged according to how much sorbate it can attract and retain in an immobilized form after conducting factorial experimental design. The amount of metal are occupied up by plant biomass was calculated as the difference between the initial and final concentrations of metal after adsorption in the aqueous solution [102, 47].

$$q = V\frac{C_i - C_f}{S}$$

where q = metal ion uptake capacity (mg g^{-1}), C_i = initial concentration of metal in solution, before the sorption analysis (mg L^{-1}), C_f = final concentration of metal in solution, after the sorption analysis (mg L^{-1}). S = dry weight of biosorbent (g) and V = aqueous solution volume (L).

Moreover, the removal efficiency was calculated according to the following equation:

$$\text{Metal removal efficiency}\,\% = \frac{C_i - C_f}{C_i} \times 100$$

where C_i is initial metal concentration in aqueous solution; C_f is final metal concentration in aqueous solutions.

7.7.1 Equilibrium and Kinetics Models

In the equilibrium modeling, empirical models such as Langmuir and Freundlich models are used. The Langmuir model makes assumptions such as monolayer adsorption and constant adsorption energy while the Freundlich model deals with heterogeneous adsorption [103].

Langmuir model is expressed by the following equation [31]:

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

where $q_{\max}$ is the maximum specific uptake corresponding to sites saturation (mg/g), b is the biomass metal-binding affinity (mg/L), and C_e is the metal residual concentration in solution (mg/L).

The feasibility of Langmuir isotherm can be expressed by a dimensionless constant separation factor [32].

$$\mathrm{SF} = \frac{1}{1 + b C_i}$$

where SF is the dimensionless equilibrium parameter or separation factor, b is Langmuir constant and C_i the initial metal ion concentration. The value of $\mathrm{SF} > 1$ indicates that biosorption is unfavorable, linear ($\mathrm{SF} = 1$), irreversible ($\mathrm{SF} < 1$), *or SF* value between 0 and 1 represents favorable biosorption.

Another equilibrium model is the Freundlich model. It is expressed as [31]:

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

where K_f is the Freundlich adsorption constant, C_e is the metal residual concentration in solution (mg/L), and $1/n$ is the measure of adsorption intensity.

Both previous equations for Langmuir and Freundlich models are used to describe the sorption of single component in aqueous solutions. Table 7.3 illustrates advantages and disadvantages of both equilibrium models.

In kinetic models, the mechanism of biosorption process is needed to be examined such as mass transfer and chemical reaction. Thus, the linear pseudo first-order equation is given as follows [31, 104]:

$$\log\left(q_{\mathrm{eq}} - qt\right) = \log \mathrm{q}_{\mathrm{eq}} - \frac{K_1}{2.303} t$$

Table 7.3 Advantages and disadvantages of equilibrium models

Equilibrium models	Pros	Cons
Langmuir model	• Has Henry law • Finite saturation limit • Valid over a wide range of concentration	• Based on monolayer assumption
Freundlich model	• Simple expression • Has a parameter for surface heterogeneity	• Does not have Henry law • No saturation limit, not structured • Not applicable over wide range of concentration

where q_{eq} and q_t are the amounts of metal ions adsorbed at equilibrium and time t (mg/g), respectively, K_1 is the rate constant of pseudo first-order adsorption process (min^{-1}).

The linear pseudo second-order equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{\mathrm{eq}}^2} + \frac{1}{q_{\mathrm{eq}}} t$$

where K_2 is the equilibrium rate constant of pseudo second-order biosorption (g/mg min).

Many researchers investigated these models. For instance, Hameed, et al. [105] studied the sorption of basic dye from aqueous solutions by banana stalk waste. Sorption models of methylene blue (MB) onto the banana stalk waste was determined at 30 °C with the initial concentrations of MB in the range of 50–500 mg/L. Equilibrium data were fitted to the Langmuir, Freundlich models. The equilibrium data were best represented by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 243.90 mg/g. The sorption kinetic data were analyzed using pseudo first-order, pseudo second-order models. It was found that the pseudo second-order kinetic model was the best applicable model to describe the sorption kinetics.

Biosorption of Pb (II) ions from aqueous solutions in a batch system using *Candida albicans* was investigated by Baysal et al. [106]. The optimum conditions of biosorption were determined by inspecting the initial metal ion concentration, contact time, temperature, biosorbent dose, and pH. Biosorption equilibrium time was observed in 30 min. The Freundlich and Langmuir adsorption models were used for the mathematical description of biosorption equilibrium, and isotherm constants were also evaluated. The maximum biosorption capacity of Pb (II) on *C. albicans* was determined as 828.50 ± 1.05, 831.26 ± 1.30, and 833.33 ± 1.12mg g−1, respectively, at different temperatures (25, 35, and 45 °C). Gupta and Rastogi [98] studied the hexavalent chromium, Cr(VI), biosorption by raw and acid-treated *Oedogonium hatei* from aqueous solutions. Batch experiments were conducted to determine the biosorption properties of the biomass. Both Langmuir and Freundlich isotherm equations could fit the equilibrium data at biomass dose of 0.8 g/L, contact time of 110 min, pH and temperature 2.0 and 318 K. Under the optimal conditions, the biosorption capacities of the raw and acid-treated algae were 31 and 35.2 mg Cr(VI) per g of dry adsorbent, respectively.

Hamissa et al. [107] investigated the potential of *Agave americana* fibers for Pb(II) and Cd(II) removal from aqueous solutions. Batch experiments were conducted as a function of pH, initial metal concentration, and temperature. Metal sorption followed pseudo second-order kinetics with excellent correlation. The Langmuir model and pseudo second-order kinetics were successfully applied to describe the sorption models. The maximum sorption capacity of *Agave americana* fibers was 40.0 mg.g^{-1} for Pb(II) and 12.5 mg g^{-1} for Cd(II), respectively, at 20 °C, pH5.0, contact time of 30–60 min and 5 g/L biomass concentration. Sometimes, these empirical models do not reflect any mechanisms of sorbate uptake and hardly have a meaningful physical interpretation for biosorption. Some authors have pointed out that the results from the empirical models cannot be extrapolated, and no predictive conclusions can be drawn for systems operating under different conditions [4].

7.7.2 Factorial Experimental Design

When we talk about factorial experimental design, we need to highlight the following expressions and definitions.

- *Factor*: a controllable experimental variable thought to influence response (as such metal ion concentration, temperature, biomass dose, flow rate of wastewater…).
- *Levels*: specific value of the studied factors (high value "+1" and low value "−1").
- *Response*: the outcome or result (e.g., metal removal efficiency from aqueous samples).
- *Interaction factors*: factors may not be independent, therefore combinations of factors may be important. If you have interaction effects, you cannot find the optimum conditions using OFAT (One Factor at a Time).

Thus, factorial experimental design is employed to define the most important factors affecting the metal removal efficiency as well as how the effect of one factor varies with the level of the other factors [108, 109]. The effect of a factor is defined as the change in response produced by a change in level of the factor. This is frequently called a main effect as it refers to the primary factors of interest in the experiment [108]. In addition the total number of experiments to be carried out in the factorial experimental design is much lower than the univariate procedure. It can reduce time and overall research cost [50, 110].

The factorial experimental design is associated with the following questions:

A. What factors should be involved in the design?
B. How many levels of each factor should be involved?
C. Which experimental units should be selected?
D. How can a factorial design be assessed to fit a real model?

The simplest factorial design involves two factors at two levels. The one-factor-at-a-time (OFAT) design is shown in Fig. 7.3a. However, Fig. 7.3b shows the points for the factorial designs that are starting with low levels and ending with high levels [111].

For example, full 2^3 factorial design requires only 8 runs versus 16 for an OFAT experiment. Hence, the ratio of the number of observations needed in a one-at-a-time experiment to the number required in a full 2^k factorial experiment grows linearly according to the following equation [112] and Fig. 7.4.

$$\frac{k+1}{2}$$

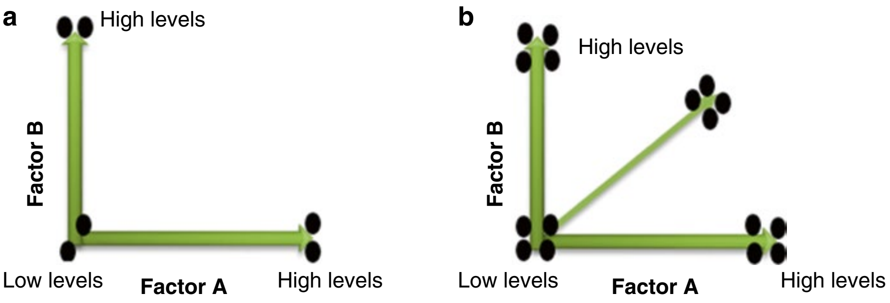

Fig. 7.3 (**a**) One-factor-at-a-time (OFAT), (**b**) two-level factorial design

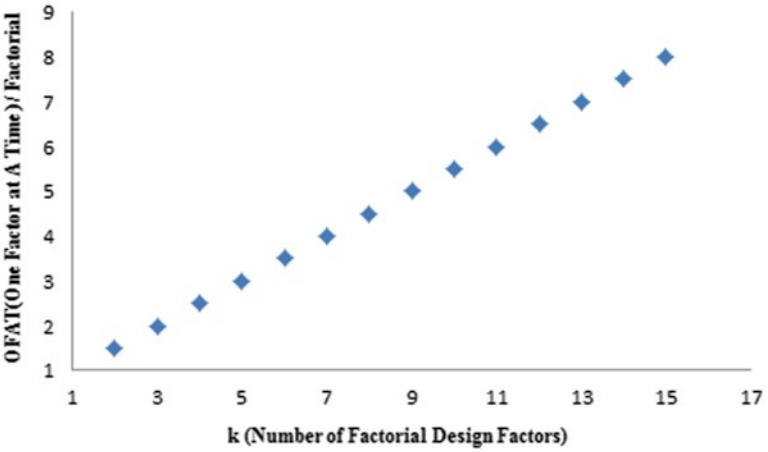

Fig. 7.4 Relative efficiency of one-at-a-time and factorial design

where *k* represents the number of factors in factorial design (Fig. 7.4).

Two levels of the three and four factors can be used, high level “+1” and low level “−1” (Tables 7.4 and 7.5). High level “+1” and low level “−1” can be changed to any numeric or text value according to the studied factors. In a full factorial experiment, responses are measured at all combinations of the factor levels. The combination of factor levels represents the conditions at which responses will be measured [113].

The codified mathematical model employed for the (2^3) factorial design is:

$$Y = A + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_1x_2 + a_5x_1x_3 + a_6x_2x_3 + a_7x_1x_2x_3$$

While the codified mathematical model employed for the (2^4) factorial design is:

$$Y = A + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_5x_1x_2 + a_6x_1x_3 + a_7x_1x_4 + a_8x_2x_3 \\ + a_9x_2x_4 + a_{10}x_3x_4 + a_{11}x_1x_2x_3x_4$$

Table 7.4 Possible interactions of the factors levels (2^3) without replication

Interaction of factors levels (2^3)			
Number of experiments	Factor 1	Factor 2	Factor 3
1	−1	−1	−1
2	−1	−1	+1
3	−1	+1	−1
4	−1	+1	+1
5	+1	−1	−1
6	+1	−1	+1
7	+1	+1	−1
8	+1	+1	+1

where Y: Estimated value or estimation of the response, A: represents the global mean (constant), a: coefficients, x: experimental variables or factors that affect biosorption process.

Coefficients could be positive or negative value. The positive sign of the coefficient represents a synergistic effect, while a negative sign indicates an antagonistic effect for the studied factors [114]. As a result, agricultural wastes/by-products have been investigated as biosorbents for the optimum removal of heavy metals from aqueous solutions by a number of researchers. Based on the literature survey, optimization of heavy metals removal from wastewater has increased in the last 14 years as illustrated in Fig. 7.5.

Badr [26] studied the removal of Cd^{2+} and Pb^{2+} by *Eichhornia crassipes* from synthetic wastewater using factorial experimental design (2^3). Experiments were carried out at two markedly different levels of three factors: pH (2.0 and 6.0), temperature (T) (20 and 45 °C), and metal ion concentration (X) (10 and 1200 mg/L). Maximum removal was observed near pH = 6 for Cd^{2+} while that for Pb^{2+} was observed near pH = 2. The most significant effect for Cd^{2+} and Pb^{2+} biosorption by *Eichhornia crassipes* was ascribed to pH and the interaction effects of T. pH and X. pH that have a significant influence on the Cd^{2+} and Pb^{2+} removal efficiency. The best removal percentage of Cd^{2+} was 85.0 % when pH = 6, X = 10 mg/L, and T = 20 °C while for Pb^{2+}, it was 84.0 % when pH = 2, X = 1200 mg/L, and T = 20 °C.

The potential of *Phragmites australis* biomass for the removal of Cd^{2+} and Pb^{2+} from synthetic wastewater using factorial design (2^3) was studied by Fawzy [16]. Experiments were carried out at two markedly different levels of three factors: pH (2.0 and 6.0), temperature (T) (20 and 45 °C), and metal ion concentration (X) (10 and 1200 mg/L). The most significant effect for Cd^{2+} and pb^{2+} biosorption was ascribed to pH. The interaction effects of T pH and T X have a significant influence on the Cd^{2+} removal efficiency while, the main Cr(VI) into Cr(III) in acidic medium. These studies were conducted at initial concentration 100 mg/L and 32 ± 0.5 °C with constant amount of biomass (0.15 g) at the constant pH6 ± 0.1 (except for Hg and Cu at pH5.5 ± 0.1). Maximum removal percentage for Pb, Hg, Cd, Cu, Zn, Co, Mn, Ni, and Cr(VI) were 81 %, 49.65 %, 21.6 %, 16.2 %, 11.20 %, 12.75 %, 11.55 %, 7.65 %, and 78.15 %, respectively. Garg et al. [115] studied the removal of Cd^{2+} from

Table 7.5 Possible interactions of the factors levels (2^4) without replication

Interaction of factors levels (2^4)				
Number of experiments	Factor 1	Factor 2	Factor 3	Factor 4
1	+1	+1	−1	−1
2	−1	−1	−1	+1
3	+1	−1	−1	+1
4	−1	+1	+1	−1
5	−1	+1	−1	+1
6	−1	−1	+1	−1
7	−1	+1	+1	+1
8	−1	−1	−1	−1
9	−1	−1	+1	+1
10	−1	+1	−1	−1
11	+1	+1	−1	+1
12	+1	−1	+1	−1
13	+1	+1	+1	−1
14	+1	−1	−1	−1
15	+1	+1	+1	+1
16	+1	−1	+1	+1

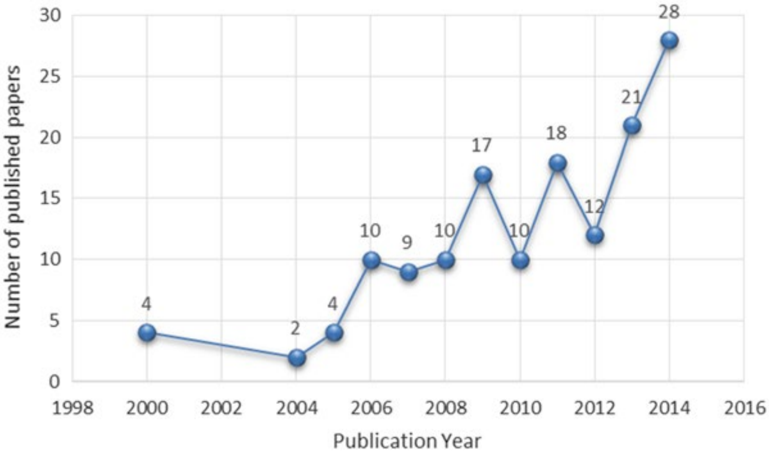

Fig. 7.5 Number of journal papers related to "optimization of heavy metals removal from wastewater" published between 2000 and 2014 (*Source*: Scopus)

aqueous solutions using sugarcane bagasse (SCB), maize corncob (MCC) and Jatropha oil cake (JOC). Batch experiments were carried out at various pH (2–7) and biosorbent dose (0.25–2 g) for a contact time of 1 h. The maximum adsorption of Cd^{2+} ions was observed at pH = 6 and dose= 2 g with percentage of 99.5 %, 99 % and 85 % for JOC, MCC, and SCB, respectively. The changes in FT-IR spectra confirmed the complexation of Cd^{2+} with functional groups present in the adsorbents.

Krishnani et al. [116] studied the sorption of eight metal ions Pb, Hg, Cd, Cu, Zn, Co, Mn and Ni by rice husk as a function of pH and metal concentrations and also for the reduction of Cr(VI) into Cr(III) in acidic medium. These studies were conducted at initial concentration 100 mg/l and 32 ± 0.5 °C with constant amount of biomass (0.15 g) at the constant pH 6 ± 0.1 (except for Hg and Cu at pH 5.5 ± 0.1). Maximum removal percentage for Pb, Hg, Cd, Cu, Zn, Co, Mn, Ni and Cr(VI) were 81 %, 49.65 %, 21.6 %, 16.2 %, 11.20 %, 12.75 %, 11.55 %, 7.65 % and 78.15 %, respectively.

Singh et al. [10] investigated the optimum environmental conditions for biosorption of Pb^{2+}, Cd^{2+}, and Cu^{2+} by *Trichoderma viride* using response surface methodology. The design variables of Box–Behnken for biosorption include: initial metal ions concentration ($X = 20–100$ mg/L), pH was selected (2–6), biomass dose ($D = 0.25–0.125$ g), and temperature ($T = 20–40$ °C). The removal of the metal ions increases with an increase in the biomass dose for all the metals ions containing 60 mg/L and pH = 4 of each of the investigated metals. The biosorption capacity of biosorbent increased with the increase in initial metal ions concentrations at the initial low temperature. At higher metal ions concentration uptake of the ions did not further increase with an increase of initial metal ions concentration resulting from the saturation of biosorbent surface. The removal decreases at higher metals ions due to the competing of the ions for the available binding site. The best removal percentage of Pb^{2+}, Cd^{2+}, and Cu^{2+} is 78.16, 76, and 63 % at $X = 60$, 20, and 60 mg/L; pH = 4, 4, and 6; $D = 0.125$, 0.125, and 0.075 g; and $T = 40$, 30, and 20 °C, respectively.

Varma et al. [113] studied the removal of cadmium from aqueous solutions using *Psidium guajava* leaves powder. The experiments were designed by 3–1 fractional factorial design. The factors in this study are metal concentration (50, 100, 150 mg/L), pH of aqueous metal solution (2, 4, and 6), and biomass dose (0.25, 0.5, and 0.75 g). Other variables such as speed of shaker adjusted at 160 rpm, volume of the aqueous solution 50 mL, and temperature 30 °C, and optimum agitation time 60 min were kept constant. The removal percentage of Cd^{2+} was 95.11 % at initial concentration = 90 mg/L, pH = 4, and biomass dose = 1 g. The increase in pH resulted in an increase in Cd uptake. Authors found that low sorption of Cd^{2+} in the $pH < 4$. This could be due to the competition with the H ions for metal-binding sites on the biomass cells, while the increase in pH favors metal sorption mainly because of negatively charged groups.

Park et al. [117] determined optimal condition for the Cr(VI) removal. Several factors such as pH, temperature, and contact time were studied. The removal efficiency of Cr (VI) increased with a decrease in pH or with an increase in temperature and contact time until equilibrium had been attained. Meanwhile, the total Cr removal efficiency increased with an increase of temperature and contact time till 60 h. Thus, 100 % of Cr (VI) removal and ~95 % of total Cr removal could be obtained at pH4 and 40 °C.

Seolatto et al. [3] studied the removal of lead, cadmium, and chromium by the Pequi Fruit Skin (*Caryocar brasiliense Camb.*) biomass and considered factors such as biomass dose (0.15, 0.75 g), pH (3, 5), and biomass size (0.2, 0.7 mm) that were studied using a factorial statistical design. The results showed that Pb^{2+} ions recorded the highest biosorption with an average of 16.78 mg/g and up to 80 % removal percentage. However, there was less removal of chromium and cadmium. The dose of biomass and pH were found to be the most important factors in the biosorption while grain size did not influence the biosorption process. Sulaymon et al. [118] studied biosorption of cadmium ions from simulated wastewater using rice husk with 100 mL of Cd^{2+} solution (concentration = 25 mg/L). The pH of the solutions was adjusted to the pH = 6 using 0.1 M NaOH or 0.1 M HNO_3. Highest removal efficiency (97 %) was obtained at 2.5 g of adsorbent, pH6, and contact time = 100 min.

Al-Qahtani [119] studied the biosorption of Cd^{2+} and Pb^{2+} on *Cyperus laevigatus* using the factorial design (2^3). The three factors were screened at two markedly different levels were pH (2.0 and 6.0), temperature (T) (20 and 45 °C), and metal ion concentration (X) (20 and 800 mg/L). The most significant effect for Cd^{2+} and Pb^{2+} biosorption was ascribed to (T). The best percentage of Cd^{2+} removal was 85 % when pH = 2, T = 45 °C, and X = 800 mg/L, but the best percentage of Pb^{2+} removal was 82 % when pH = 6, T = 45 °C, and X = 20 mg/L. Muhammad and Nwaedozie [120] studied the removal of lead and cadmium using marine algae-seaweed (*Ascophyllum nodosum*) as adsorbent for metal removal at two temperatures (23.5 °C and 37 °C) and four pH values (2, 5, 7, and 10). The maximum removal of lead was 93.41 % at pH2 and 53.13 % for cadmium at pH10. Temperature was found to have no significant effect on the adsorption process.

The biosorption efficiency of Cd^{2+} using rice straw was investigated by Nasr et al. [114]. Experiments studied the effect of three factors, biosorbent dose BD (0.1 and 0.5 g/L), pH (2 and 7), and initial Cd^{2+} concentration X (10 and 100 mg/L) at two levels "low" and "high." From 2^3 factorial design, the effects of BD, pH, and X achieved p value equals to 0.2248, 0.1881, and 0.1742, respectively, indicating that the influences are in the order $X > \text{pH} > \text{BD}$. Mahmoud et al. [47] investigated the removal of Cd^{2+} by dragon tree leaves using full factorial design. Results revealed that the optimum results (79.60 %) was attained at metal ion concentration = 10 ppm, pH = 7, and biomass dose = 0.5 g.

7.8 Quality Control/Quality Assurance

When biosorption experiments are conducted, errors can be occurred. These errors are due to cross-contamination from glassware or used chemicals and metal ions loss owing to sorption or volatilization [121, 122]. To reduce or prevent these errors, acidification of pH between 1 and 2 has been done to prevent metabolism by microorganisms and hydrolysis and precipitation. Also, cooling and freezing for reduction of bacterial activity and water samples should be stored in darkness and kept refrigerated (–4 °C) until the completion of analysis. Moreover, the shortest time between the sampling and the analysis increases the reliability of analytical results[123].

In this investigation, metal solutions should be stored in polyethylene bottles till their metal content was analyzed. Polyethylene or Teflon bottles are used in inorganic analysis to minimize loss of metal ions on their surfaces [124]. Also, metal solution samples were acidified down to pH ~ 2 (with HNO_3) till analyses. It has been recommended to acidify the sample down to pH ~ 2 to avoid adsorption on plastic bottle and prevents precipitation of metal hydroxides or adsorption of metal ions on the walls of the bottle. We will give some examples below.

7.8.1 Cleaning Glassware and Plastic Bottles

Glassware and plastic bottles must be washed with detergent overnight immersed in 10 % HNO_3 and rinsed with double distilled water (DDW) several times.

7.8.2 Blanks

Samples of metal solutions should be used without biosorbents to determine initial metal concentration.

7.8.3 Replicates

All experiments and measurements should be conducted in duplicates or triplicates.

7.9 Recommendations

Eco-friendly treatment processes for wastewater are major fundamentals for a developing and growing economy of developing countries. Therefore, it is crucial to implement such treatment processes. It is known that the environmental-based market for metal removal from industrial effluents is enormous [125]. So it is mandatory to apply economic analyses especially for the design of eco-friendly treatment plants [126]. As a result, when the adsorption process is considered, the kind of the used adsorbent is regarded as the most critical factor both on removal efficiency and total operational costs [126]. In general, the low-cost biosorbent should be [14]:

A. Efficient to remove many and different contaminants
B. Have high adsorption capacity and rate of adsorption
C. Have high selectivity for different concentrations.

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