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# 5 Removal of Heavy Metals by Low-Cost Adsorption Materials

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## ABSTRACT

Owing to the environmental impact as well as the growing awareness among the public, it is imperative to remove or reduce the concentration of heavy metals to environmentally acceptable levels before being discharged to open stream. The conventional methods for removing heavy metals suffer from many drawbacks such as high cost, sludge disposal problem, complex technology, and limited applicability. Therefore, intensive research has been carried out using low-cost materials to remove these heavy metals at an affordable cost. This chapter examines (i) some commonly found heavy metals in wastewater, (ii) main treatment technologies and their limitations, (iii) various studies using waste materials from agriculture and industry or naturally occurring biosorbents, (iv) chemical properties and characterization studies on the low-cost adsorbents, (v) influential parameters in affecting the removal efficiency, and (vi) equilibrium, kinetic models, and process design used in the adsorption process.

## 5.1 HEAVY METALS

Wastewater may be defined as a combination of liquid and water-transported wastes from homes, commercial buildings, industrial facilities, and institutions along with any groundwater infiltration, surface water, and stormwater inflow that may enter the sewer system. The rapid growth of human population and industrialization in the world has resulted in increased wastewater generation. This kind of waste may contain various pollutants such as heavy metals, toxic organic compounds, phosphorus, detergents, biodegradable organics, nutrients, dissolved inorganic solids, and refractory organics.

Amongst all, heavy metals pose one of the most serious environmental problems and one of the most difficult to solve. The term “heavy metals” is misleading because they are not all “heavy” in terms of atomic weight, density, or atomic number. Besides, they are not even entirely metallic in character, for example, arsenic. As a rough generalization, the heavy metals include all the metals in the periodic table except those in Groups I and II (I). Heavy metals such as mercury, lead, arsenic, chromium, copper, cadmium, and nickel are widely used in industry, particularly in metal finishing or metal-plating industries and in products such as batteries and electronic devices. Nevertheless, the technologically important heavy metals also cause increasing environmental hazards. Table 5.1 shows the concentrations of leachate contaminants found in the petroleum, calcium fluoride, and metal finishing industrial sludges.

Wastewater containing heavy metals has been of great concern due to their toxicity and carcinogenic effect. Even very small amounts can cause severe physiological or neurological damage. Thus, numerous ways have been attempted to prevent or minimize this kind of potential health hazard. This includes government regulations, research to develop methods for waste treatment by scientists, and revision of the technologies used in industries to produce degradable wastes or disposal of wastes in ways less damaging to the environment and human beings.

### 5.1.1 CHROMIUM

Chromium (Cr) was discovered in 1797 by the French chemist Louis N. Vauquelin in the rare mineral crocoite ( $\text{PbCrO}_4$ ). It was named for the varied colors of its compounds (chroma = color) (3).

**TABLE 5.1**  
**Concentrations of Specific Cations, Anions, and Organics in the**  
**Three Industrial Sludge Leachates (m/L)**

| Measured <sup>a</sup><br>Pollutant | Acidic<br>Petroleum<br>Sludge Leachate | Neutral Calcium<br>Fluoride Sludge<br>Leachate | Basic Metal<br>Finishing Sludge<br>Leachate |
|------------------------------------|--|--|---|
| Ca                                 | 34–50                                  | 180–318  | 31–38                                       |
| Cu                                 | 0.09–0.17                              | 0.10–0.16                                      | 0.45–0.53                                   |
| Mg                                 | 27–50                                  | 4.8–21   | 24–26                                       |
| Ni                                 | — <sup>b</sup>                         | —  | —   |
| Zn                                 | 0.13–0.17                              | —  | —   |
| F                                  | 0.95–1.2                               | 6.7–11.6                                       | 1.2–1.5                                     |
| Total CN                           | 0.20–1.2                               | —  | —   |
| COD                                | 251–340                                | 44–49  | 45–50                                       |

Source: US Environmental Protection Agency. 1980. *Evaluation of Sorbents for Industrial Sludge Leachate Treatment*, EPA-600/2-80-052. US EPA, Cincinnati, OH.

<sup>a</sup> Fe, Cd, Cr, and Pb contents were analyzed, but found to be below measurable levels.

<sup>b</sup> Dashed line indicated amounts below measurable levels.

It is a naturally occurring element which is commonly found in rocks, minerals, and sources of geologic emissions such as volcanic dusts and gases. Chromium has atomic number 24. There are 13 known isotopes of chromium (mass number 45–47) in which four are stable, giving chromium the relative atomic mass 51.9961. Although chromium can exist in several chemical forms displaying oxidation numbers from 0 to VI, only two of them: trivalent chromium, Cr(III) and hexavalent chromium Cr(VI), are stable enough to occur in the environment (4).

Cr(VI), a Lewis base, is water soluble and always exists in solution as a component of a complex anion. Basically, the speciation of Cr(VI) is concentration and pH dependent. At pH <1, the dominant species is chromic acid ( $H_2CrO_4$ ); while the equilibrium between monohydrogen chromate ion ( $HCrO_4^-$ ) and dichromate ion ( $Cr_2O_7^{2-}$ ) occurs at pH 2–6. Meanwhile, chromate ion ( $CrO_4^{2-}$ ) presents as the major component with a pH above 6.

Chromium is usually found in industrial effluents because of their widespread usage in a variety of commercial processes. Chromium and its compounds are used in metal alloys such as stainless steel; protective coatings on metal; magnetic tapes; and pigments for paints, cement, paper, rubber, composite floor covering and other materials. Other uses include chemical intermediate for wood preservatives, organic chemical synthesis, photochemical processing, and industrial water treatment. In medicine, chromium compounds are used in astringents and antiseptics whereas they serve as catalysts and fungicides in the leather tanning industry. Chromium is also found application in brewery processing and brewery warmer water where it acts as an algacide against slime forming bacteria and yeasts (5).

Since Cr(VI) is able to penetrate through cell membranes efficiently and undergoes strong oxidation, making it a serious environmental pollutant which may represent a considerable health risk (4). Acute high exposure levels cause skin ulceration, perforation of the nasal septum, gastrointestinal irritation, kidney and liver damage as well as internal hemorrhage (5,6). Cr(VI) compounds are also found to produce a variety of genotoxic effects, including DNA damage, mutations, and chromosomal aberrations, in both *in vitro* and *in vivo* test systems (7). The United State Public Health Service has estimated the upper limit from lifetime exposure to 1 mg/L Cr(VI) to result in 120 additional cases of cancer in a population of 10,000 (6).

### 5.1.2 COPPER

Copper (Cu) is a crystalline reddish metal, with an atomic number of 29 and atomic weight of 63.55. It exists mainly in four valence states, that is, Cu(0), Cu(I), Cu(II), and Cu(III) of which Cu(II) is the most common and stable ion (8). It is easily complexed and is involved in many metabolic processes in living organisms. Copper is among the 25 most abundant elements in the Earth's crust, occurring at about 50–100 g/ton, and has played an important role in human technological, industrial, and cultural development since primitive times. Copper is also distinguished by several properties which contribute to its extensive use: (i) a combination of mechanical workability with corrosion resistance to many substances, (ii) excellent electrical conductivity, (iii) superior thermal conductivity, (iv) efficient as an ingredient of alloys to improve their physical and chemical properties, (v) capable as catalysts for several kinds of chemical reaction, (vi) nonmagnetic characteristics, advantageous in electrical and magnetic apparatus, and (vii) nonsparking characteristics, mandatory for tools for use in explosive atmosphere (9).

Copper is one of the few common metals that find greater commercial applications as pure metal rather than in alloys. The major uses of copper are building construction (roofing parts and gutters) and plumbing installation (valves and pipe fittings), electrical and electronics products (wire, motors, generators, and cable), and household appliances (radios and television sets). Apart from these, it is also used in the production of alloys with zinc, nickel, and tin, as catalysts and in the electrochemical industry. Copper salts are useful as pigments, fungicides, and biocides as well as in various pharmaceutical uses. For instance, copper chromate is used as pigments, catalysts for liquid-phase hydrogenation, and as potato fungicides (10).

Copper is also an essential element nutritionally, being among the most abundant metallic elements in the human body, which is needed in many protein and enzymes (i.e., ferroxidases, cytochrome oxidase, superoxide dismutase, and amine oxidases). However, like all heavy metals, intake of excessively large doses of copper by humans will cause severe health disorders such as liver and renal damage, gastrointestinal irritation, anemia, and central nervous system irradiation. Long-term exposure can lead to copper poisoning, especially in people whose bodies have trouble regulating copper because of certain genetic disorders or illness, such as Wilson's disease (11).

### 5.1.3 CADMIUM

Cadmium (Cd) is a soft, bluish-white metal with an atomic number of 48. It is similar in many respects to zinc (prefers the oxidation state of +2) and mercury (shows low-melting point compared with other transition metals). Cadmium is a metal widely used in industries such as cadmium plating, alkaline batteries, copper alloys, paints, and plastics. Its high resistance to corrosion makes it applicable as a protective layer when it is deposited on other metals.

Most of the Cd compounds released to the environment are contained in solid wastes form (e.g., coal ash, sewage sludge, flue dust, and fertilizers). Cd has been well recognized for its negative effect on the environment where it accumulates throughout the food chain, posing a serious threat to human health. The extremely long biological half-life of Cd also causes a major concern.

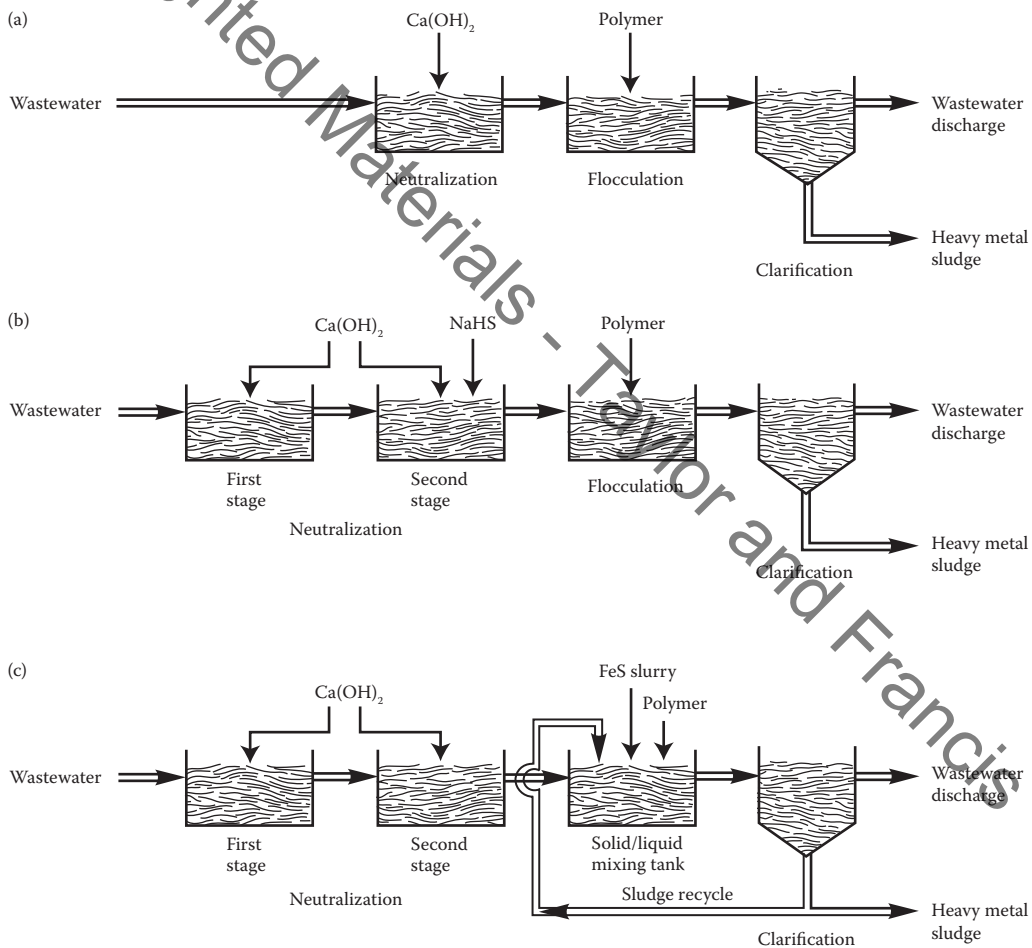
Toxic effects of cadmium on humans include both chronic and acute disorders such as testicular atrophy, hypertension, damage to kidneys and bones, anemia, itai-itai, and so on. It has been recorded that the intake of Cd-contaminated rice led to itai-itai disease and renal abnormalities, including proteinuria and glucosuria.

Cd is also found in cigarette smoke and long-term inhalation of CdO dust could cause a syndrome characterized by damage to the pulmonary and renal systems. Acute Cd poisoning may lead to lung edema, in some cases with lethal outcome.

## 5.2 TREATMENT OF HEAVY METALS

### 5.2.1 CHEMICAL PRECIPITATION

Chemical precipitation is perhaps the oldest and the most widely used method for the removal of heavy metals from wastewater. This method can be considered as a low-cost and effective process for the removal of large quantities of metal ion. Precipitation involves the formation of an insoluble compound from a solution upon addition of a properly selected reagent. The most commonly used chemicals are lime or caustic for hydroxide precipitation, sodium sulfide or sodium hydrosulfide for sulfide precipitation and sodium bicarbonate for carbonate precipitation. Figure 5.1 illustrates the different designs of hydroxide precipitation, soluble sulfide precipitation (SSP), and insoluble sulfide precipitation (ISP) processes in the wastewater treatment systems. The precipitate can then be separated from the wastewater using some physical separation process, such as sedimentation, coagulation, and filtration. Table 5.2 presents the comparison of metal per liter of raw feed before treatment and wastewater after treatment using five variations of chemical precipitation techniques.



**FIGURE 5.1** Wastewater treatment processes for removing heavy metals in the electroplating industry: (a) hydroxide precipitation, (b) SSP, and (c) ISP. (From US Environmental Protection Agency. 1980. *Control and Treatment Technology for the Metal Finishing Industry Sulfide Precipitation*, EPA-625/8-80-003. US EPA, Cincinnati, OH.)

**TABLE 5.2**  
**Chemical Analysis of Raw and Treated Wastewater Used in Pilot Tests**

| Contaminant (µg/L)  | Raw Feed<br>Before<br>Treatment | Wastewater After Treatment <sup>a</sup> |        |        |        |       |
|---------------------|---------------------------------|---|--------|--------|--------|-------|
|                     |                                 | LO-C                                    | LO-CF  | LWS-C  | LWS-CF | LSPF  |
| <b>Pilot Test 1</b> |                                 |   |        |        |        |       |
| Cadmium             | 45                              | 15                                      | 8      | 11     | 7      | 20    |
| Total chromium      | 163,000                         | 3,660                                   | 250    | 1,660  | 68     | 159   |
| Copper              | 4,700                           | 135                                     | 33     | 82     | 18     | 3     |
| Nickel              | 185                             | 30                                      | 38     | 33     | 31     | 18    |
| Zinc                | 2,800                           | 44                                      | 10     | 26     | 2      | 11    |
| Lead                | 119                             | 119                                     | 88     | 104    | 59     | 120   |
| <b>Pilot Test 2</b> |                                 |   |        |        |        |       |
| Cadmium             | 58                              | 7                                       | 12     | <5     | <5     | <5    |
| Total chromium      | 6,300                           | 4                                       | 2      | 5      | 7      | 3     |
| Hexavalent chromium | 5                               | <1                                      | <1     | <1     | <1     | <1    |
| Copper              | 1,100                           | 860                                     | 848    | 13     | 13     | 132   |
| Nickel              | 160                             | 30                                      | 34     | 33     | 23     | 34    |
| Zinc                | 650,000                         | 2,800                                   | 2,300  | 104    | 19     | 242   |
| Mercury             | <1                              | NA                                      | NA     | NA     | NA     | NA    |
| Silver              | 16                              | NA                                      | NA     | NA     | NA     | NA    |
| <b>Pilot Test 3</b> |                                 |   |        |        |        |       |
| Cadmium             | 34                              | 21                                      | 21     | 1      | 1      | 1     |
| Total chromium      | 3                               | NA                                      | NA     | NA     | NA     | NA    |
| Copper              | 20                              | 7                                       | 8      | 2      | 1      | 4     |
| Nickel              | 64                              | 29                                      | 29     | 72     | 34     | 31    |
| Zinc                | 440,000                         | 37,000                                  | 29,000 | 730    | 600    | 2,000 |
| Mercury             | <10                             | NA                                      | NA     | NA     | NA     | NA    |
| Lead                | 45                              | 13                                      | 14     | 9      | 11     | 13    |
| Silver              | 61                              | 4                                       | 4      | 1      | 3      | 4     |
| Tin                 | 200                             | <10                                     | <10    | <10    | <10    | <10   |
| Ammonium            | ( <sup>b</sup> )                | NA                                      | NA     | NA     | NA     | NA    |
| <b>Pilot Test 4</b> |                                 |   |        |        |        |       |
| Cadmium             | 58,000                          | 1,130                                   | 923    | 26     | <10    | <10   |
| Total chromium      | 5,000                           | 138                                     | 103    | 49     | 50     | 37    |
| Copper              | 2,000                           | 909                                     | 943    | 60     | 160    | 929   |
| Nickel              | 3,000                           | 2,200                                   | 2,300  | 1,800  | 1,900  | 2,600 |
| Zinc                | 290,000                         | 1,200                                   | 510    | 216    | 38     | 12    |
| Iron                | 740,000                         | 2,000                                   | 334    | 563    | 229    | 305   |
| Mercury             | <0.3                            | <0.3                                    | <0.3   | <0.3   | <0.3   | <0.3  |
| Silver              | 14                              | 14                                      | 10     | 7      | 7      | 8     |
| Tin                 | 5,000                           | 129                                     | 81     | 71     | 71     | 71    |
| <b>Pilot Test 5</b> |                                 |   |        |        |        |       |
| Cadmium             | <40                             | <1                                      | <1     | <1     | <1     | <1    |
| Total chromium      | 1,700                           | 109                                     | 39     | 187    | 17     | 20    |
| Copper              | 21,000                          | 1,300                                   | 367    | 2,250  | 169    | 11    |
| Nickel              | 119,000                         | 12,000                                  | 9,400  | 11,000 | 3,500  | 5,300 |

(Continued)

TABLE 5.2 (Continued)

## Chemical Analysis of Raw and Treated Wastewater Used in Pilot Tests

| Contaminant ( $\mu\text{g/L}$ ) | Raw Feed         | Wastewater After Treatment <sup>a</sup> |       |       |        |      |
|---------------------------------|------------------|---|-------|-------|--------|------|
|                                 | Before Treatment | LO-C                                    | LO-CF | LWS-C | LWS-CF | LSPF |
| Zinc                            | 13,000           | 625                                     | 10    | 192   | 8      | 5    |
| Iron                            | NA               | 2                                       | <2    | 5     | <2     | <2   |
| Lead                            | 13               | 7                                       | 5     | 4     | 3      | 3    |
| Silver                          | 6                | NA                                      | NA    | NA    | NA     | NA   |

Source: US Environmental Protection Agency. 1980. *Control and Treatment Technology for the Metal Finishing Industry Sulfide Precipitation*, EPA-625/8-80-003. US EPA, Cincinnati, OH.

Note: Wastewater by pilot test: 1—high chromium rinse from aluminum cleaning, anodizing, and electroplating; 2—chromium, copper, and zinc rinse from electroplating; 3—high zinc rinse from electroplating; 4 and 5—mixed heavy metal rinse from electroplating.

<sup>a</sup> LO-C = lime only, clarified; LO-CF = lime only, clarified, filter; LWS-C = lime with sulfide, clarified; LWS-CF = lime with sulfide, clarified, filtered; LSPF = lime, sulfide polished, filtered; and NA = not applicable.

<sup>b</sup> Qualitative tests indicated the presence of significant amounts of ammonium.

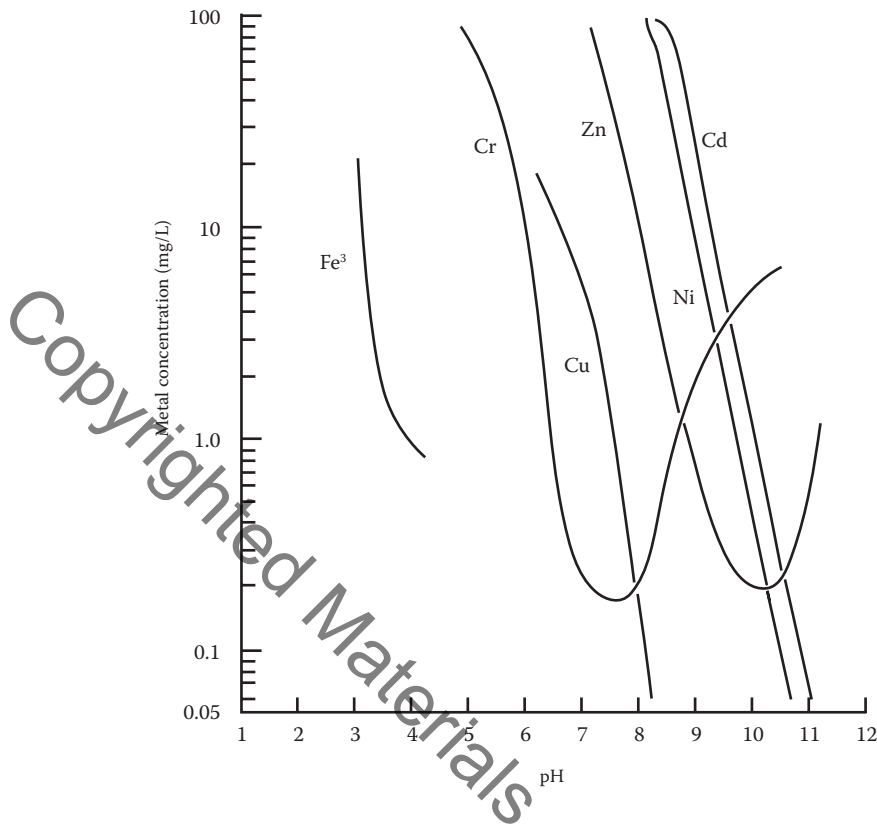
Although this process has wide applicability in the removal of toxic metals from aqueous waste, still, there are limitations need to be addressed. For instance, chemical precipitation is not applicable when the metal of interest is highly soluble and does not precipitate out of solution at any pH such as Cr(VI). Consequently, treatment of Cr(VI) usually consists of a two-stage process: the reduction of Cr(VI) to Cr(III) using sulfur dioxide gas from sodium bisulfate solution, followed by the precipitation of Cr(III) (13). This method is not favorable since it does not allow complete recovery of chromium in the desired hexavalent oxidation state.

For hydroxide precipitation, it requires certain pH in order to reduce metal concentration to that below the level required by standards. This is very difficult to achieve if the solution contains multiple metals as the pH of minimum solubility varies from metal to metal. Figure 5.2 shows the theoretical minimum solubilities for different metals occur at different pH values. For sulfide precipitation, the limitations are the evolution of sulfide gas and discharge of excess soluble sulfide. Nevertheless, sulfide precipitation still appears to be a better alternative compared with hydroxide for removing heavy metals from wastewater. This is mainly attributed to the attractive features of sulfide such as high reactivity (reaction between  $\text{S}^{2-}/\text{HS}^-$  with heavy metal ions) and insolubility of metal sulfides over a broad pH range (12). Other limitation of chemical precipitation is the need to use excess amounts of chemical for precipitation to avoid resolubilization of any precipitated compound after filtration thereby implying it is costly. Besides, the disposal of sludge produced during chemical precipitation has created another environmental problem. The generated sludges are hazardous and require a special storage facility and specific treatment before disposal. Table 5.3 lists the characteristics of the wastewater before treatment (hydroxide precipitation, SSP), the volume of sludge generated and the amount of chemical reagents consumed in the treatment. The ultimate disposal of these significant quantities of sludges and large amounts of reagents consumed may be very expensive and indirectly increase the cost of treatment.

### 5.2.2 ION EXCHANGE

Ion exchange is a chemical treatment process used to remove the dissolved ionic species from contaminated aqueous streams. It involves the reversible exchange of ions in solution with the ions held





**FIGURE 5.2** Metal solubility as a function of pH. (From US Environmental Protection Agency, 1973. *Waste Treatment: Upgrading Metal-Finishing Facilities to Reduce Pollution*, EPA-625/3-73-002. US EPA, Cincinnati, OH.)

by a solid ion-exchanging material, in which there is no directly perceptible permanent change in the structure of the solid. Ion exchangers are generally utilized in column reactors so that a high degree of exchanger utilization is achieved. They can be characterized by a number of physical properties including particle size, density, degree of cross-linking, resistance to oxidation, and thermal stability.

Ion exchange resin can be broadly classified as strong or weak cation exchangers and strong or weak anion exchangers. Table 5.4 shows the capacity of ion exchangers and cost of ion-exchange operation for metal recovery. The classification of the resins is based on the active ion-exchange sites of the resin, for example, strong acid cation exchange resin possesses sulfonic groups; weak acid cation exchange resin generally contains carboxylic acid groups; strong base anion exchange possesses quaternary ammonium groups while weak base anion exchange resin contains functional groups that are derived from weak base amines, such as tertiary ( $-NR_2$ ), secondary ( $-NHR$ ), or primary ( $-NH_2$ ) amino groups. Chelating resins behave similar to weak acid cation resins but exhibit a high degree of selectivity for metal cations over sodium, calcium, or magnesium.

Soluble heavy metals, which are amenable to treatment by ion exchange include arsenic, barium, cadmium, chromium, cyanide, mercury, selenium, and silver. The advantage of ion-exchange technique is put to use in the treatment of wastewater without generating sludge. Besides, it permits the reuse of rinse water in a close cycle and recovery of metal in the wastewater. However, regardless of the efficiency of ion-exchange resins for heavy metal removal, the cost incurred (Table 5.4) prohibits the treatment of highly concentrated wastewater; it is thereby typically used as a polishing step after precipitation.



**TABLE 5.3**  
**Wastewater Treatment Process Details of Pilot Tests**

| Characteristic                                   | Pilot Test <sup>a</sup> |                 |                  |               |               |
|--|-------------------------|-----------------|------------------|---------------|---------------|
|  | 1                       | 2 <sup>b</sup>  | 3                | 4             | 5             |
| <b>Raw feed before treatment</b>                 |                         |                 |                  |               |               |
| pH   | 1.7                     | 1.2             | 6.4              | 2.4           | 7.1           |
| Conductivity ( $\mu\text{mho}/\text{cm}$ )       | 10,600 at 70°F          | 149,000 at 68°F | 12,100 at 77°F   | 5,600 at 66°F | 1,500 at 70°F |
| Color  | Yellow                  | Colorless       | Colorless        | Colorless     | Pale green    |
| <b>Precipitation pH for LO and LWS processes</b> | 8.5                     | 6.2/9.0         | 9.0              | 10.0          | 8.5           |
| <b>Sludge volume (%)<sup>c</sup></b>             |                         |                 |                  |               |               |
| LO process                                       | 18                      | 78/23           | ( <sup>d</sup> ) | 43            | 5             |
| LWS process                                      | 16                      | 78/13           | ( <sup>d</sup> ) | 37            | 6             |
| <b>Process consumables (mg/L)</b>                |                         |                 |                  |               |               |
| Sulfuric acid for Cr <sup>6+</sup> reduction     | 0                       | 0               | 0                | 0             | 339           |
| Sodium sulfite for Cr <sup>6+</sup> reduction    | 226                     | 31              | 0                | 41            | 25            |
| Calcium oxide for neutralization                 | 1,530                   | 14,380          | 911              | 2,680         | 145           |
| Sulfide for LWS process                          | 8                       | 381             |                  | 400           | 91            |
| Sulfide for LPSF process                         | 1                       | 5               |                  | 141           | 67            |

Source: US Environmental Protection Agency, 1980. *Control and Treatment Technology for the Metal Finishing Industry Sulfide Precipitation*, EPA-625/8-80-003, US EPA, Cincinnati, OH.

Note: LO = lime only; LWS = lime with sulfide; and LPSF = lime, sulfide polished, filtered.

<sup>a</sup> Wastewater by pilot test: 1—high chromium rinse from aluminum cleaning, anodizing, and electroplating; 2—chromium, copper, and zinc rinse from electroplating; 3—high zinc rinse from electroplating; 4 and 5—mixed heavy metal rinse from electroplating.

<sup>b</sup> Because of the exceptionally large volume of sludge generated by this wastewater, precipitation was accomplished in two stages. First- and second-stage values are separated by a diagonal line; single values apply to the total process.

<sup>c</sup> Sludge volume per solution volume, percent after 1 h settling.

<sup>d</sup> Data not available.

### 5.2.3 MEMBRANE SYSTEM

One of the growing interests in the reduction and/or recycling of hazardous waste involves the use of membrane separation processes. These processes include reverse osmosis, electrodialysis, hyperfiltration, and ultrafiltration. Reverse osmosis is a pressure-driven membrane process in which a feed stream containing inorganic ions under the pressure is separated into a purified permeated stream and a concentrate stream. The pure water is forced through a semipermeable membrane into the less concentrated solution and the flow stops when equal concentrations are attained on both sides of the membrane, at which point the solvent molecules pass through the membrane in both directions at equal rates. The most commonly used membrane materials are cellulose acetate, aromatic polyamides, and thin film composites. One of the major applications of reverse osmosis has been in the recovery of metals from the effluents generated by the electroplating plants, which have been engaged in electroplating nickel, copper, brass, and cadmium.

Ultrafiltration and hyperfiltration utilize pressure and a semipermeable membrane to separate nonionic materials from the solvent. These membrane separation techniques are particularly effective for the removal of suspended solid, oil, and grease, large organic molecules, and heavy metal complexes from the wastewater stream.

Electrodialysis is used for the separation, removal, or concentration of ionized species in aqueous solutions by the selective transport of ions through ion-exchange membranes under the influence

**TABLE 5.4**  
**Ion Exchange Capacity and Cost of Ion Exchange Operation for Metal Recovery**

| Metal Form                     | Cation Exchange                |                 | Metal Form                     | Anion Exchange                 |                 |
|--------------------------------|--------------------------------|-----------------|--------------------------------|--------------------------------|-----------------|
|                                | Capacity (lb/ft <sup>3</sup> ) | Cost (cents/lb) |                                | Capacity (lb/ft <sup>3</sup> ) | Cost (cents/lb) |
| Al <sub>2</sub> O <sub>3</sub> | 1.1                            | 14              | Sb                             | 4.5                            | 6.7             |
| BeO                            | 0.5                            | 30              | Bi                             | 3.1                            | 9.7             |
| Cd                             | 6.7                            | 2.3             | Cr <sub>2</sub> O <sub>3</sub> | 1.9                            | 16              |
| Ce <sub>2</sub> O <sub>3</sub> | 5.6                            | 2.7             | Ga                             | 5.2                            | 5.8             |
| CsCl                           | 16.0                           | 9.4             | Ge                             | 5.4                            | 5.6             |
| CoO                            | 3.6                            | 4.2             | Au                             | 7.3                            | 4.1             |
| Cu                             | 3.8                            | 3.9             | Ha                             | 6.6                            | 4.9             |
| Pb                             | 12.4                           | 1.2             | Ir                             | 7.1                            | 4.2             |
| LiO                            | 0.8                            | 18              | Mo                             | 3.6                            | 8.4             |
| Mg                             | 1.5                            | 10              | Nb                             | 3.4                            | 8.8             |
| MgO                            | 1.5                            | 10              | Pd                             | 3.9                            | 7.8             |
| Mn                             | 3.3                            | 4.6             | Pt                             | 7.2                            | 4.2             |
| Hg                             | 12                             | 13              | Re                             | 13.8                           | 2.2             |
| Ni                             | 3.5                            | 4.3             | Rh                             | 2.9                            | 10              |
| Ra                             | 13.6                           | 11              | Ta                             | 6.7                            | 4.5             |
| Rare earths                    | 6.3                            | 2.4             | ThO <sub>2</sub>               | 8.6                            | 3.5             |
| Ag                             | 13                             | 1.2             | W <sub>2</sub> O <sub>3</sub>  | 6.8                            | 4.4             |
| Sn                             | 7.1                            | 2.1             | V <sub>2</sub> O <sub>5</sub>  | 3.8                            | 7.9             |
| Zn                             | 3.9                            | 38              | UO <sub>2</sub>                | 8.8                            | 3.4             |
|                                |                                |                 | Zr                             | 3.4                            | 8.8             |

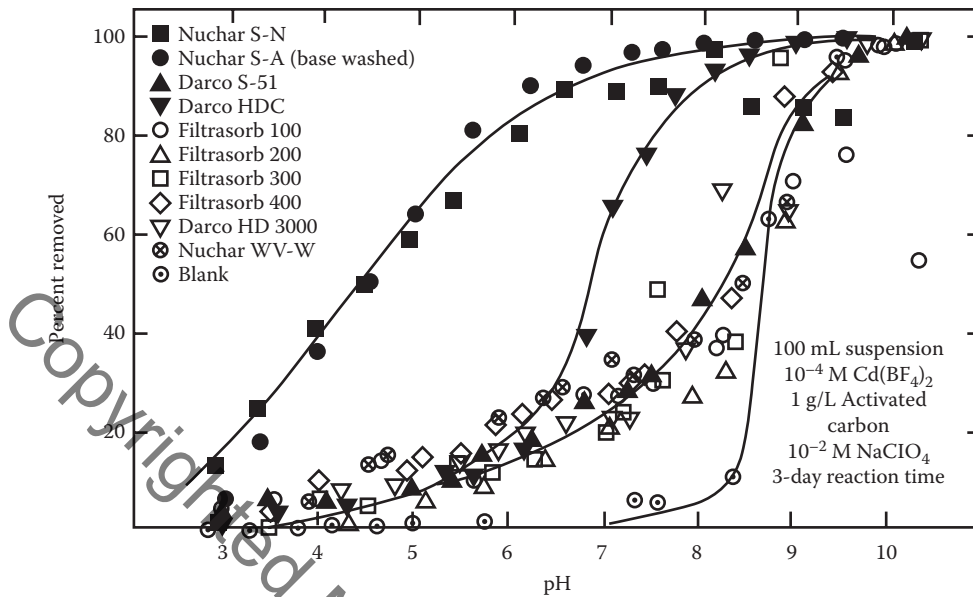
Source: US Environmental Protection Agency. 1973. *Traces of Heavy Metals in Water Removal Processes and Monitoring*, EPA-902/9-74-001. US EPA, Cincinnati, OH.

of an electrical potential across the membrane. Depending on the ion-exchange material, the membranes are permeable to either anions or cations, but not both. These membranes allow the ions to transfer through them from a less concentrated to a more concentrated solution.

A membrane system can be used for the removal of heavy metal ions but the concentration of metal ions in the feed stream has to be reasonably low for a successful operation of a membrane process. With the increasing concentration of metals in the feed streams, the rejection of the membrane is lowered and a membrane scaling is often noted. This shows an increase in the process cost but a decline in process efficiency. In addition, membranes used in the process are considerably expensive materials, a fact that is aggravated by their relative short operation life. Membranes are subjected to deterioration in the presence of microorganism, compaction, scaling, and loss of productivity with time. As such, this system remains as an expensive treatment option and requires a high level of technical expertise to operate.

#### 5.2.4 ADSORPTION

Adsorption is an attachment of the molecules of a gas or a liquid to the surface of another substance (usually solid); these molecules form a closely adherent film or layer held in place by different attractive forces. The three defined forces are physical, chemical, and electrostatic interactions. Physical adsorption results from the action of van der Waals forces; chemical adsorption involves electronic interactions between specific surface sites and solute molecules; an electrostatic interaction is generally reserved for Coulombic attractive forces between ions and charged functional groups.



**FIGURE 5.3** Typical cadmium(II) removal of different types of activated carbons as affected by pH. (From US Environmental Protection Agency, 1983. *Activated Carbon Process for the Treatment of Cadmium(II)-Containing Wastewaters*, EPA/600/S2-83-06). US EPA, Cincinnati, OH.)

Activated carbon, both in granular and powder form, is recognized as one of the most well-known adsorbents. Granular-activated carbons are widely used in flow through column reactors for carbon adsorption systems. Figure 5.3 exemplifies the effect of 17 different types of commercial activated carbons on Cd(II) removal. The adsorption properties of activated carbon are primarily a result of its highly porous structure, or equivalently the high specific surface area of the finished product. This kind of adsorption process is reversible and it is usually used in removing the adsorbed contaminants after the adsorption capacity of the carbon has been exhausted.

The applications of activated carbon adsorption for heavy metals have also been well documented. However, it is ineffective for very low concentrations. Another drawback of activated carbon adsorption in heavy metal removal is its high affinity toward organic molecules. Thus, in the presence of any high molecular-weight compounds, the internal pores in the deep regions of the bed are blocked and unavailable to adsorb contaminants. Besides, the activation process and regeneration of activated carbon require high capital investment. The heat treatment and activation process must be repeated after every regeneration process following the elution of saturated carbon. Apart from that, the carbon suffers from weight loss and reduction in adsorption capacity by approximately 10%–15% after each regeneration process. Another problem associated with the carbon adsorbent is the development of excessive head loss as a result of suspended solid accumulation, biological growth in the bed, or fouling of the influent screen.

### 5.2.5 BIOSORPTION

Generally, all biological materials have certain biosorptive ability. In this case, biosorption can be considered as a new sorption process developed for the removal of toxic metal ions from wastewater. This kind of sorption process involves the removal of metal or metalloids species, compounds, and particulates by biological materials through passive sorption. Tables 5.5 through 5.7 present the removal capacities of biosorbents, nonbiosorbents, and activated carbons for treating sludge leachates from petroleum, calcium fluoride, and metal finishing industries, respectively.

TABLE 5.5

Net Sorbent Removal Capacities for Treating Acidic Petroleum Sludge Leachate ( $\mu\text{g/g}$ )<sup>a</sup>

| Pollutant       | Acidic Fly Ash | Basic Fly Ash | Zeolite | Vermiculite | Illite | Kaolinite | Activated Alumina | Activated Carbon |
|-----------------|----------------|---------------|---------|-------------|--------|-----------|-------------------|------------------|
| Ca              | 0              | 0             | 1,390   | 686         | 721    | 10.5      | 200               | 128              |
| Cu              | 2.4            | 1.9           | 5.2     | 1.1         | 0      | 0         | 0.35              | 0                |
| Mg              | 0              | 102           | 746     | 67          | 110    | 595       | 107               | 8.6              |
| Zn              | 1.6            | 1.7           | 10.8    | 4.5         | 0      | 0         | 0.40              | 1.1              |
| F <sup>-</sup>  | 8.7            | 6.2           | 4.1     | 0           | 9.3    | 3.5       | 3.4               | 1.2              |
| CN <sup>-</sup> | 2.7            | 2.5           | 4.7     | 7.6         | 12.1   | 3.1       | 0                 | 2.4              |
| COD             | 3,818          | 3,998         | 468     | 6,654       | 4,807  | 541       | 411               | 3,000            |
| TOC             | 1,468          | 737           | 170     | 2,545       | 2,175  | 191       | 176               | 1,270            |

Source: US Environmental Protection Agency. 1980. *Evaluation of Sorbents for Industrial Sludge Leachate Treatment*, EPA-600/2-80-052. US EPA, Cincinnati, OH.

Note: +Cl<sup>-</sup>, Cd, Cr, Fe, Ni, and Pb were measured and found in low concentrations.

<sup>a</sup>  $\mu\text{g}$  of contaminant removed/g of sorbent used.

TABLE 5.6

Net Sorbent Removal Capacities for Treating Neutral Calcium Fluoride Sludge Leachate ( $\mu\text{g/g}$ )<sup>a</sup>

| Pollutant      | Acidic Fly Ash | Basic Fly Ash | Zeolite | Vermiculite | Illite | Kaolinite | Activated Alumina | Activated Carbon |
|----------------|----------------|---------------|---------|-------------|--------|-----------|-------------------|------------------|
| Ca             | 261            | 0             | 5054    | 0           | 0      | 857       | 6140              | 357              |
| Cu             | 2.1            | 0.36          | 8.2     | 0           | 0      | 6.7       | 2.9               | 2.0              |
| Mg             | 230            | 155           | 0       | 0           | 0      | 0         | 214               | 3.0              |
| F <sup>-</sup> | 102            | 51.8          | 27.7    | 0           | 175    | 132       | 348               | 0                |
| COD            | 690            | 203           | 171     | 0           | 108    | 185       | 0                 | 956              |
| TOC            | 153            | 44.7          | 93      | 0           | 264    | 71        | 0                 | 325              |

Source: US Environmental Protection Agency. 1980. *Evaluation of Sorbents for Industrial Sludge Leachate Treatment*, EPA-600/2-80-052. US EPA, Cincinnati, OH.

Note: +Cl<sup>-</sup>, CN<sup>-</sup>, Cd, Cr, Cu, Fe, Ni, Pb, and Zn were measured and found in low concentrations.

<sup>a</sup>  $\mu\text{g}$  of contaminant removed/g of sorbent used.

Biomass raw materials (e.g., seaweed and algae) or wastes from other industrial operations (e.g., fungi from fermentation process) serve as attractive sources of biosorbents. Table 5.8 illustrates the Freundlich constants for sorption of four heavy metals, which adequately described the removal efficiency of the filamentous fungi. The cell wall of the biosorbents which consists of mainly polysaccharides, proteins, and lipids is capable of concentrating heavy metal ions, known as bioaccumulation. Furthermore, the presence of many functional groups such as carboxylate, hydroxyl, sulfate, phosphate, and amino groups which can bind metal ions is also considered as an added feature for this kind of biosorbent.

The interaction between biosorbents and metal can occur via complexation, coordination, chelation, ion exchange, adsorption, and inorganic microprecipitation. Any one or combination of the mentioned metal binding mechanisms may be subjected to various degrees in immobilizing one or more metallic species on the biosorbent.

Some of the advantages of biosorption worth mentioning include its (i) ability to bind heavy metal ions in the presence of commonly encountered ions such as calcium, magnesium, sodium, chloride, sulfate, and potassium without interference; (ii) efficiency in metal removal and is often

**TABLE 5.7**  
**Net Sorbent Removal Capacities for Treating Basic Metal Finishing Sludge Leachate ( $\mu\text{g/g}$ )<sup>a</sup>**

| Pollutant      | Acidic Fly Ash | Basic Fly Ash | Zeolite | Vermiculite | Illite | Kaolinite | Activated Alumina | Activated Carbon |
|----------------|----------------|---------------|---------|-------------|--------|-----------|-------------------|------------------|
| Ca             | 87.3           | 97.8          | 1,240   | 819         | 1280   | 735       | 737               | 212              |
| Cu             | 13.0           | 6.1           | 85.4    | 15.2        | 43.1   | 23.7      | 6.2               | 16.8             |
| Mg             | 296            | 176           | 1,328   | 344         | 1,122  | 494       | 495               | 188              |
| Ni             | 3.8            | 1.7           | 13.5    | 2.3         | 5.1    | 4.6       | 2.3               | 4.7              |
| F <sup>-</sup> | 0              | 0             | 2.1     | 0           | 2.2    | 2.6       | 11.4              | 0                |
| COD            | 1,080          | 259           | 0       | 618         | 1,744  | 0         | 0                 | 1,476            |
| TOC            | 430            | 115           | 0       | 244         | 729    | 0         | 0                 | 589              |

Source: US Environmental Protection Agency. 1980. *Evaluation of Sorbents for Industrial Sludge Leachate Treatment*, EPA-600/2-80/052. US EPA, Cincinnati, OH.

Note: +Cl, CN, Cd, Cr, Fe, Pb, and Zn were measured and found in low concentrations.

<sup>a</sup>  $\mu\text{g}$  of contaminant removed/g of sorbent used.

comparable with commercial ion exchangers; and (iii) role in improving a zero-waste economic policy especially in the case of reuse of agricultural and industrial byproducts.

However, the capability of biosorbents in metal removal is greatly affected by several factors. These include the specific surface properties of the biosorbents and physicochemical parameters of the solution, for instances, temperature, pH, initial metal ion concentration, and biomass concentration. If there is more than one metal to be bound simultaneously, the combined effects would depend on metal ion combination, levels of metal concentration, and on the order of metal addition (18,19).

Some of the advantages and disadvantages of the main conventional removal of heavy metals technologies discussed above are summarized in Table 5.9. Cost of treatment is always the main consideration in choosing a suitable type of heavy metal treatment. Figure 5.4 shows the estimated total annual cost for various treatment processes in Cd(II) wastewater.

**TABLE 5.8**  
**Freundlich Constants for Heavy Metal Sorption by Filamentous Fungi**

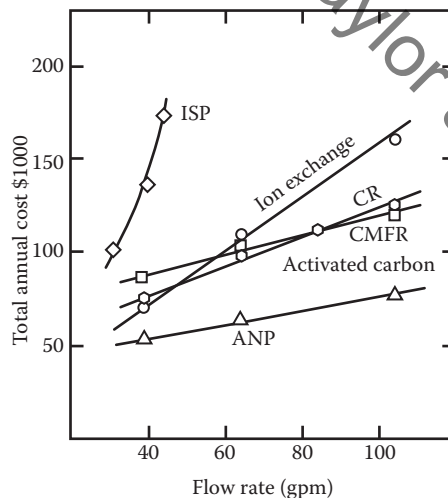
| Metal | Fungus           | <i>K</i> | <i>N</i> | <i>r</i> <sup>2</sup> |
|-------|------------------|----------|----------|-----------------------|
| Ag    | <i>A. niger</i>  | 1.096    | 0.892    | 0.953                 |
|       | <i>M. rouxii</i> | 3.373    | 0.641    | 0.806                 |
| Cd    | <i>A. niger</i>  | 0.156    | 0.679    | 0.861                 |
|       | <i>M. rouxii</i> | 0.039    | 0.875    | 0.994                 |
| Cu    | <i>A. niger</i>  | 0.889    | 0.495    | 0.921                 |
|       | <i>M. rouxii</i> | 0.746    | 0.551    | 0.963                 |
| La    | <i>A. niger</i>  | 2.877    | 0.426    | 0.971                 |
|       | <i>M. rouxii</i> | 5.702    | 0.314    | 0.968                 |

Source: US Environmental Protection Agency. 1990. *Sorption of Heavy Metals by Intact Microorganisms, Cell Walls, and Clay-Wall Composites*, EPA/600/M-90/004. US EPA, Cincinnati, OH.

Note: The constant *K* represents the amount of metal sorbed in  $\mu\text{mol/g}$  at an equilibrium concentration of 1  $\mu\text{M}$  and *n* is the slope of the log transformed isotherm.

**TABLE 5.9**  
**Comparison of Main Convectional Heavy Metals Removal Technologies**

| Technology                     | Advantages   | Disadvantages  |
|--------------------------------|--|--|
| Chemical precipitation         | <ul style="list-style-type: none"> <li>• Simple and inexpensive treatment</li> <li>• Chemicals used are easily available</li> </ul>  | <ul style="list-style-type: none"> <li>• High sludge production</li> <li>• Disposal problem</li> <li>• pH sensitive</li> <li>• Moderate metal selectivity (sulfide)</li> <li>• Nonmetal selectivity (hydroxide)</li> </ul>                         |
| Ion exchange                   | <ul style="list-style-type: none"> <li>• High regeneration of materials</li> <li>• Effective pure effluent</li> <li>• Metal selectivity</li> <li>• Metal recovery</li> </ul> | <ul style="list-style-type: none"> <li>• High cost</li> <li>• Sensitive to suspended solids</li> </ul>   |
| Membrane systems               | <ul style="list-style-type: none"> <li>• Less solid waste production</li> <li>• Pure effluent</li> <li>• Metal recovery</li> <li>• Minimal chemical consumption</li> </ul>   | <ul style="list-style-type: none"> <li>• High initial and running cost</li> <li>• Membrane scaling</li> <li>• Sensitive to suspended solids</li> <li>• High pressures</li> <li>• Efficiency decreases with the presence of other metals</li> </ul> |
| Adsorption by activated carbon | <ul style="list-style-type: none"> <li>• Removes most of the heavy metals</li> <li>• High efficiency</li> </ul>  | <ul style="list-style-type: none"> <li>• Pores blockage in the presence of high molecular-weight compounds</li> <li>• High regeneration cost</li> <li>• Weight loss and reduction in adsorption capacity</li> </ul>                                |
| Biosorption                    | <ul style="list-style-type: none"> <li>• Economically attractive, utilization of nature resources, regeneration is avoidable</li> </ul>                                      | <ul style="list-style-type: none"> <li>• Temperature, pH, initial metal ion concentration and biomass concentration dependent</li> </ul>   |



**FIGURE 5.4** Estimated total cost of various cadmium(II) treatment processes. (From US Environmental Protection Agency, 1983. *Activated Carbon Process for the Treatment of Cadmium(II)-Containing Wastewaters*, EPA/600/S2-83-061. US EPA, Cincinnati, OH.) Note: CMFR = completely mixed flow reactor-activated carbon; CR = column reactor-activated carbon; ANP = alkaline neutralization precipitation; and ISP = insoluble sulfide precipitation.

### 5.3 APPLICATION OF LOW-COST ADSORBENTS FOR HEAVY METALS REMOVAL

The need of industries to lessen the pollution loads before the discharge enters the surface water and the limitations of existing conventional methods for heavy metals removal have led to the search in developing low-cost treatment methods. Numerous techniques have been attempted; but still, adsorption is constantly viewed as a highly effective method for this purpose. The application of low-cost adsorbent materials makes this approach even more attractive and feasible. In this context, low-cost adsorbent materials can be defined as those that are generally available at free cost and are abundant in nature. Utilization of naturally occurring material or locally available agricultural waste materials, or industrial byproducts as the adsorbents for the removal of heavy metals from wastewaters offers not only an economical approach for heavy metal removal, but also other advantages such as the possibility of attaining a zero-waste situation in the environment.

A lot of investigations have been reported on using these low-cost adsorbent materials for the adsorption of individual or multiple heavy metals in an aqueous solution. Some of these adsorbents have shown excellent performance in the removal of heavy metals from industrial wastewater. In this section, some of the selected materials from industrial byproducts, agriculture waste, and bio-adsorbents were discussed in terms of their efficiency for heavy metals removal. Recent reported adsorption capacities of the selected adsorbents are presented in Tables 5.10 through 5.15 to provide some idea of adsorbent effectiveness. However, the reported adsorption capacities must be taken as values that can be attained only under specific conditions since the adsorption capacities of the adsorbents would be varied, depending on the characteristics of the adsorbent, the experimental conditions as well as the extent of chemical modifications. Thus, the reader is encouraged to refer to the original articles for a detailed information on the experimental conditions.

#### 5.3.1 FLY ASH

Fly ash, a waste from the perspective of power generation is generally gray in color, abrasive, mostly alkaline, and refractory in nature. The primary components of fly ash have been identified as alumina ( $\text{Al}_2\text{O}_3$ ), silica ( $\text{SiO}_2$ ), calcium oxide ( $\text{CaO}$ ), and iron oxide ( $\text{Fe}_2\text{O}_3$ ), with varying amounts of carbon, calcium, magnesium, and sulfur. The chemical composition and physical properties of fly ash may vary due to the variations in coals from different sources as well as differences in the design of coal-fired boilers. However, an empirical formula for fly ash based on the dominance of certain key elements has been proposed as (20)



Generally, fly ash can be classified into two types: (i) type C, which is normally produced from the burning of low-rank coals (lignites or subbituminous coals) and has cementitious properties (self-hardening upon reaction with  $\text{H}_2\text{O}$ ) and (ii) type F which is commonly produced from the burning of higher-rank coals (bituminous coals or anthracites) that is pozzolanic in nature (hardening when reacted with  $\text{Ca}(\text{OH})_2$  and  $\text{H}_2\text{O}$ ). The main difference between these two types lies on the sum of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ .

Most of the fly ash generated is disposed of as landfill, a practice which is under examination for environmental concerns. Therefore, continuing research efforts have been made to utilize this waste material into new products rather than land disposal to lessen the environmental burden. The potential applications of fly ash include as raw material in cement and brick production and as filler in road works. The conversion of fly ash into zeolite has gained considerable interest as well. Another attractive possibility might be to make it into a low-cost adsorbent for gas and water treatment provided production could match industrial needs. A lot of investigations have been reported



**TABLE 5.10**  
**Adsorption Capacities of Metals by Fly Ash<sup>a</sup>**

| Metals  | Adsorbent              | Adsorption Capacity <sup>b</sup> | Temperature (°C) | References |
|---------|------------------------|----------------------------------|------------------|------------|
| As(III) | Fly ash coal-char      | 3.7–89.2                         | 25               | 21         |
| As(V)   | Fly ash                | 7.7–27.8                         | 20               | 22         |
|         | Fly ash coal-char      | 0.02–34.5                        | 25               | 21         |
| Cd(II)  | Fly ash                | 1.6–8.0                          | –                | 23         |
|         | Fly ash zeolite        | 95.6                             | 20               | 23         |
|         | Fly ash                | 0.67–0.83                        | 20               | 24         |
|         | Afsin-Elbistan fly ash | 0.08–0.29                        | 20               | 25         |
|         | Seyitomer fly ash      | 0.0077–0.22                      | 20               | 25         |
|         | Fly ash                | 198.2                            | 25               | 26         |
|         | Fly ash-washed         | 195.2                            | 25               | 26         |
|         | Fly ash-acid           | 180.4                            | 25               | 26         |
|         | Bagasse fly ash        | 1.24–2.0                         | 30–50            | 27         |
|         | Fly ash                | 0.05                             | 25               | 28         |
|         | Coal fly ash           | 18.98                            | 25               | 29         |
|         | Coal fly ash pellets   | 18.92                            | –                | 29         |
|         | Bagasse fly ash        | 6.19                             | –                | 30         |
|         | Fly ash zeolite X      | 97.78                            | –                | 31         |
| Co(II)  | Fly ash zeolite 4A     | 13.72                            | –                | 32         |
| Cr(III) | Fly ash                | 52.6–106.4                       | 20–40            | 33         |
|         | Bagasse fly ash        | 4.35                             | –                | 34         |
|         | Fly ash zeolite 4A     | 41.61                            | –                | 32         |
| Cr(VI)  | Fly ash + wollastonite | 2.92                             | –                | 35         |
|         | Fly ash + China clay   | 0.31                             | –                | 35         |
|         | Fly ash                | 1.38                             | 30–60            | 36         |
|         | Fe impregnated fly ash | 1.82                             | 30–60            | 36         |
|         | Al impregnated fly ash | 1.67                             | 30–60            | 36         |
|         | Afsin-Elbistan fly ash | 0.55                             | 20               | 25         |
|         | Seyitomer fly ash      | 0.82                             | 20               | 25         |
|         | Bagasse fly ash        | 4.25–4.35                        | 30–50            | 34         |
|         | Fly ash                | 23.86                            | –                | 37         |
| Cs(I)   | Fly ash zeolite        | 443.9                            | 25               | 38         |
| Cu(II)  | Fly ash                | 1.39                             | 30               | 39         |
|         | Fly ash +wollastonite  | 1.18                             | 30               | 39         |
|         | Fly ash                | 1.7–8.1                          | –                | 23         |
|         | Afsin-Elbistan fly ash | 0.34–1.35                        | 20               | 40         |
|         | Seyitomer fly ash      | 0.09–1.25                        | 20               | 40         |
|         | Fly ash                | 207.3                            | 25               | 41         |
|         | Fly ash-washed         | 205.8                            | 25               | 41         |
|         | Fly ash-acid           | 198.5                            | 25               | 41         |
|         | Fly ash                | 0.63–0.81                        | 25               | 42         |
|         | Bagasse fly ash        | 2.26–2.36                        | 30–50            | 43         |
|         | Fly ash                | 0.76                             | 32               | 44         |
|         | Fly ash                | 7.5                              | –                | 41         |
|         | Coal fly ash pellets   | 20.92                            | 25               | 29         |
|         | Fly ash zeolite 4A     | 50.45                            | –                | 32         |
|         | Fly ash                | 7.0                              | –                | 45         |
|         | Coal fly ash (CFA)     | 178.5–249.1                      | 30–60            | 46         |
|         | CFA-600                | 126.4–214.1                      | 30–60            | 46         |
|         | CFA-NAOH               | 76.7–137.1                       | 30–60            | 46         |

(Continued)

**TABLE 5.10 (Continued)**  
**Adsorption Capacities of Metals by Fly Ash<sup>a</sup>**

| Metals            | Adsorbent              | Adsorption Capacity <sup>b</sup> | Temperature (°C) | References |    |
|-------------------|------------------------|----------------------------------|------------------|------------|----|
| Hg(II)            | Fly ash zeolite X      | 90.86                            | –                | 31         |    |
|                   | Fly ash                | 7.0                              | –                | 47         |    |
|                   | Fly ash                | 2.82                             | 30               | 48         |    |
|                   | Fly ash                | 11.0                             | 30–60            | 36         |    |
|                   | Fe impregnated fly ash | 12.5                             | 30–60            | 36         |    |
|                   | Al impregnated fly ash | 13.4                             | 30–60            | 36         |    |
|                   | Sulfo-calcic fly ash   | 5.0                              | 30               | 41         |    |
|                   | Silico-aluminous ashes | 3.2                              | 30               | 41         |    |
| Ni(II)            | Fly ash-C              | 0.63–0.73                        | 5–21             | 49         |    |
|                   | Fly ash                | 9.0–14.0                         | 30–60            | 50         |    |
|                   | Fe impregnated fly ash | 9.8–14.93                        | 30–60            | 50         |    |
|                   | Al impregnated fly ash | 10–15.75                         | 30–60            | 50         |    |
|                   | Afsin-Elbistan fly ash | 0.40–0.98                        | 20               | 40         |    |
|                   | Seyitomer fly ash      | 0.06–1.16                        | 20               | 40         |    |
|                   | Bagasse fly ash        | 1.12–1.70                        | 30–50            | 27         |    |
|                   | Fly ash                | 3.9                              | –                | 41         |    |
|                   | Fly ash zeolite 4A     | 8.96                             | –                | 32         |    |
|                   | Afsin-Elbistan fly ash | 0.98                             | –                | 25         |    |
|                   | Seyitomer fly ash      | 1.16                             | –                | 25         |    |
|                   | Bagasse fly ash        | 6.48                             | –                | 30         |    |
|                   | Fly ash                | 0.03                             | –                | 51         |    |
|                   | Pb(II)                 | Fly ash zeolite                  | 79.6             | 20         | 52 |
| Fly ash           |                        | 444.7                            | 25               | 53         |    |
| Fly ash-washed    |                        | 483.4                            | 25               | 53         |    |
| Fly ash-acid      |                        | 437.0                            | 25               | 53         |    |
| Fly ash           |                        | 753                              | 32               | 53         |    |
| Bagasse fly ash   |                        | 285–566                          | 30–50            | 54         |    |
| Fly ash           |                        | 18.8                             | –                | 22         |    |
| Fly ash zeolite X |                        | 420.61                           | –                | 31         |    |
| Zn(II)            |                        | Fly ash                          | 6.5–13.3         | 30–60      | 50 |
|                   |                        | Fe impregnated fly ash           | 7.5–15.5         | 30–60      | 50 |
|                   | Al impregnated fly ash | 7.0–15.4                         | 30–60            | 50         |    |
|                   | Fly ash                | 0.25–2.8                         | 20               | 24         |    |
|                   | Afsin-Elbistan fly ash | 0.25–1.19                        | 20               | 40         |    |
|                   | Seyitomer fly ash      | 0.07–1.30                        | 20               | 40         |    |
|                   | Bagasse fly ash        | 2.34–2.54                        | 30–50            | 43         |    |
|                   | Bagasse fly ash        | 13.21                            | 30               | 55         |    |
|                   | Fly ash                | 4.64                             | 23               | 56         |    |
|                   | Fly ash                | 0.27                             | 25               | 28         |    |
|                   | Fly ash                | 0.068–0.75                       | 0–55             | 57         |    |
|                   | Fly ash                | 3.4                              | –                | 41         |    |
|                   | Fly ash zeolite 4A     | 30.80                            | –                | 32         |    |
|                   | Bagasse fly ash        | 7.03                             | –                | 30         |    |
|                   | Fly ash                | 11.11                            | –                | 47         |    |
|                   | Rice husk ash          | 14.30                            | –                | 58         |    |
| Fly ash           | 7.84                   | –                                | 47               |            |    |

<sup>a</sup> These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions.

<sup>b</sup> In mg/g.

**TABLE 5.11**  
**Adsorption Capacities of Metals by Rice Husk <sup>a</sup>**

| Metals  | Adsorbent  | Adsorption Capacity <sup>b</sup> | Temperature (°C) | References |
|---------|--|----------------------------------|------------------|------------|
| As(III) | Copolymer of iron and aluminum impregnated with active silica derived from rice husk ash | 146                              | –                | 61         |
| As(V)   | Rice husk  | 615.11                           | –                | 62         |
|         | Quaternized rice husk  | 18.98                            | –                | 63         |
| Au(I)   | Rice husk  | 64.10                            | 40               | 64         |
|         | Rice husk  | 50.50                            | 30               | 64         |
|         | Rice husk  | 39.84                            | 20               | 64         |
|         | Rice husk ash  | 21.2                             | –                | 65         |
| Cd(II)  | Partial alkali digested and autoclaved rice husk   | 16.7                             | –                | 66         |
| Cd(II)  | Phosphate-treated rice husk  | 103.09                           | 20               | 67         |
|         | Rice husk  | 73.96                            | –                | 68         |
|         | Rice husk  | 21.36                            | –                | 62         |
|         | Rice husk  | 4                                | –                | 69         |
|         | Rice husk  | 8.58 ± 0.19                      | –                | 70         |
|         | Rice husk  | 0.16                             | –                | 71         |
|         | Rice husk  | 0.32                             | –                | 72         |
|         | NaOH treated rice husk   | 125.94                           | –                | 68         |
|         | NaOH treated rice husk   | 7                                | –                | 69         |
|         | NaOH treated rice husk   | 20.24 ± 0.44                     | –                | 70         |
|         | NaHCO <sub>3</sub> treated rice husk   | 16.18 ± 0.35                     | –                | 70         |
|         | Epichlorohydrin treated rice husk  | 11.12 ± 0.24                     | –                | 70         |
|         | Rice husk ash  | 3.04                             | –                | 73         |
|         | Polyacrylamide grafted rice husk   | 0.889                            | –                | 74         |
|         | HNO <sub>3</sub> , K <sub>2</sub> CO <sub>3</sub> treated rice husk                      | 0.044 ± 0.1 <sup>c</sup>         | 30               | 75         |
|         | Partial alkali digested and autoclaved rice husk   | 9.57                             | –                | 66         |
| Cr(III) | Rice husk  | 1.90                             | –                | 72         |
|         | Rice husk ash  | 240.22                           | –                | 76         |
| Cr(VI)  | Rice husk  | 164.31                           | –                | 62         |
|         | Rice husk  | 4.02                             | –                | 71         |
|         | Rice husk ash  | 26.31                            | –                | 37         |
|         | Rice husk-based activated carbon   | 14.2–31.5                        | –                | 77         |
|         | Formaldehyde treated rice husk   | 10.4                             | –                | 78         |
|         | Preboiled rice husk  | 8.5                              | –                | 78         |
| Cu(II)  | Tartaric acid modified rice husk   | 29                               | 27               | 79         |
|         | Tartaric acid modified rice husk   | 22                               | 50               | 79         |
|         | Tartaric acid modified rice husk   | 18                               | 70               | 79         |
|         | Tartaric acid modified rice husk   | 31.85                            | –                | 80         |
|         | Rice husk heated to 500°C (RHA500)   | 16.1                             | –                | 81         |
|         | Rice husk  | 1.21                             | –                | 72         |
|         | Rice husk  | 0.2                              | –                | 73         |
|         | Rice husk  | 7.1                              | –                | 81         |
|         | Rice husk ash  | 11.5191                          | –                | 82         |
|         | RH-cellulose   | 7.7                              | –                | 81         |
|         | Rice husk heated to 300°C (RHA300)   | 6.5                              | –                | 81         |
|         | Microwave incinerated rice husk ash (800°C)  | 3.497                            | –                | 83         |
|         | Microwave incinerated rice husk ash (500°C)  | 3.279                            | –                | 83         |
|         | HNO <sub>3</sub> , K <sub>2</sub> CO <sub>3</sub> treated rice husk                      | 0.036 ± 0.2 <sup>c</sup>         | 30               | 75         |

(Continued)

**TABLE 5.11 (Continued)**  
**Adsorption Capacities of Metals by Rice Husk<sup>a</sup>**

| Metals    | Adsorbent  | Adsorption Capacity <sup>b</sup> | Temperature (°C) | References |
|-----------|--|----------------------------------|------------------|------------|
| Fe(II)    | Partial alkali digested and autoclaved rice husk   | 10.9                             | –                | 66         |
|           | Copolymer of iron and aluminum impregnated with active silica derived from rice husk ash | 222                              | –                | 61         |
| Hg(II)    | Rice husk ash  | 6.72                             | 30               | 84         |
|           | Rice husk ash  | 9.32                             | 15               | 84         |
|           | Rice husk ash  | 40.0–66.7                        | –                | 85         |
|           | Polyaniline/rice husk ash nanocomposite  | Not determined                   | –                | 86         |
| Mn        | Partial alkali digested and autoclaved rice husk   | 36.1                             | –                | 66         |
|           | Copolymer of iron and aluminum impregnated with active silica derived from rice husk ash | 158                              | –                | 61         |
| Ni(II)    | Partial alkali digested and autoclaved rice husk   | 8.30                             | –                | 66         |
|           | Rice husk  | 0.23                             | –                | 72         |
|           | Rice husk ash  | 4.71                             | –                | 87         |
|           | Microwave-irradiated rice husk (MIRH)  | 1.17                             | 30               | 88         |
| Pb(II)    | Partial alkali digested and autoclaved rice husk   | 5.52                             | –                | 66         |
|           | Rice husk ash  | 12.61                            | 30               | 84         |
|           | Rice husk ash  | 12.35                            | 15               | 84         |
|           | HNO <sub>3</sub> , K <sub>2</sub> CO <sub>3</sub> treated rice husk                      | 0.058 ± 0.1 <sup>c</sup>         | 30               | 75         |
|           | Rice husk ash  | 207.50                           | –                | 89         |
|           | Rice husk ash  | 91.74                            | –                | 90         |
|           | Copolymer of iron and aluminum impregnated with active silica derived from rice husk ash | 416                              | –                | 61         |
|           | Tartaric acid modified rice husk   | 120.48                           | –                | 79         |
|           | Tartaric acid modified rice husk   | 108                              | 27               | 79         |
|           | Tartaric acid modified rice husk   | 105                              | 50               | 79         |
|           | Tartaric acid modified rice husk   | 96                               | 70               | 79         |
|           | Partial alkali digested and autoclaved rice husk   | 58.1                             | –                | 66         |
|           | Tartaric acid modified rice husk   | 21.55                            | –                | 69         |
|           | Rice husk  | 6.385                            | 25               | 91         |
| Rice husk | 5.69   | 30                               | 92               |            |
| Rice husk | 45   | –                                | 69               |            |
| Rice husk | 11.40  | –                                | 62               |            |
| Zn(II)    | HNO <sub>3</sub> , K <sub>2</sub> CO <sub>3</sub> treated rice husk                      | 0.037 ± 0.2 <sup>c</sup>         | 30               | 75         |
|           | Rice husk  | 30.80                            | 50               | 93         |
|           | Rice husk  | 29.69                            | 40               | 93         |
|           | Rice husk  | 28.25                            | 30               | 93         |
|           | Rice husk  | 26.94                            | 20               | 93         |
|           | Rice husk ash  | 14.30                            | –                | 68         |
|           | Rice husk ash  | 7.7221                           | –                | 82         |
|           | Rice husk ash  | 5.88                             | –                | 73         |
|           | Partial alkali digested and autoclaved rice husk   | 8.14                             | –                | 66         |
|           | Rice husk  | 0.75                             | –                | 72         |
|           | Rice husk  | 0.173                            | –                | 71         |

<sup>a</sup> These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions.

<sup>b</sup> In mg/g except in footnote c.

<sup>c</sup> In mmol/g.

**TABLE 5.12**  
**Adsorption Capacities of Metals by Wheat-Based Materials<sup>a</sup>**

| Metals  | Adsorbent                       | Adsorption Capacity <sup>b</sup> | References |
|---------|---------------------------------|----------------------------------|------------|
| Cd(II)  | Wheat straw                     | 14.56                            | 94         |
|         | Wheat straw                     | 11.60                            | 95         |
|         | Wheat straw                     | 40.48                            | 96         |
|         | Wheat bran                      | 51.58                            | 97         |
|         | Wheat bran                      | 15.71                            | 98         |
|         | Wheat bran                      | 21.0                             | 99         |
|         | Wheat bran                      | 101                              | 100        |
| Cr(III) | Wheat straw                     | 21.0                             | 101        |
|         | Wheat bran                      | 93.0                             | 99         |
| Cr(VI)  | Wheat straw                     | 47.16                            | 96         |
|         | Wheat bran                      | 35                               | 102        |
|         | Wheat bran                      | 40.8                             | 103        |
|         | Wheat bran                      | 310.58                           | 104        |
|         | Wheat bran                      | 0.942                            | 105        |
| Cu(II)  | Wheat straw                     | 11.43                            | 94         |
|         | Wheat straw citric acid treated | 78.13                            | 106        |
|         | Wheat bran                      | 12.7                             | 107        |
|         | Wheat bran                      | 17.42                            | 108        |
|         | Wheat bran                      | 8.34                             | 109        |
|         | Wheat bran                      | 6.85                             | 110        |
|         | Wheat bran                      | 51.5                             | 111        |
|         | Wheat bran                      | 15.0                             | 99         |
| Hg(II)  | Wheat bran                      | 70.0                             | 99         |
| Ni(II)  | Wheat straw                     | 41.84                            | 96         |
|         | Wheat bran                      | 12.0                             | 99         |
| Pb(II)  | Wheat bran                      | 87.0                             | 112        |
|         | Wheat bran                      | 62.0                             | 99         |
|         | Wheat bran                      | 79.4                             | 100        |
| Zn(II)  | Wheat bran                      | 16.4                             | 107        |
| U(VI)   | Wheat straw                     | 19.2–34.6                        | 113        |

<sup>a</sup> These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions.

<sup>b</sup> In mg/g.

on the use of fly ash in the adsorption of individual pollutants in an aqueous solution or flue gas. The results obtained when using these particular fly ashes are encouraging for the removal of heavy metals and organics from industrial wastewater. Adsorption capacities of fly ash for the removal of metals are provided in Table 5.10.

### 5.3.2 RICE HUSK

Rice is grown on every continent except Antarctica and ranks second only to wheat in terms of worldwide area and production. When rough rice or paddy rice is husked, rice husk is generated as a waste and generally, every 100 kg of paddy rice produces 20 kg of husk. Of course, the rice husk

**TABLE 5.13**  
**Adsorption Capacities of Metals by Chitosan and Chitosan Composites<sup>a</sup>**

| Adsorbent   | Metal   | Adsorption Capacity <sup>b</sup> | Temperature (°C) | References |
|---|---------|----------------------------------|------------------|------------|
| Chitosan/cotton fibers (via Schiff base bond)               | Hg(II)  | 104.31                           | 35               | 114        |
| Chitosan/cotton fibers (via C–N single bond)                | Hg(II)  | 96.28                            | 25               | 114        |
| Chitosan/cotton fibers (via Schiff base bond)               | Cu(II)  | 24.78                            | 25               | 115        |
| Chitosan/cotton fibers (via Schiff base bond)               | Ni(II)  | 7.63                             | 25               | 115        |
| Chitosan/cotton fibers (via Schiff base bond)               | Pb(II)  | 101.53                           | 25               | 115        |
| Chitosan/cotton fibers (via Schiff base bond)               | Cd(II)  | 15.74                            | 25               | 115        |
| Chitosan/cotton fibers (via Schiff base bond)               | Au(III) | 76.82                            | 25               | 116        |
| Chitosan/cotton fibers (via C–N single bond)                | Au(III) | 88.64                            | 25               | 116        |
| Magnetic chitosan   | Cr(VI)  | 69.40                            | –                | 117        |
| Chitosan/magnetite  | Pb(II)  | 63.33                            | –                | 118        |
| Chitosan/magnetite  | Ni(II)  | 52.55                            | –                | 118        |
| Chitosan/cellulose  | Cu(II)  | 26.50                            | 25               | 119        |
| Chitosan/cellulose  | Zn(II)  | 19.81                            | 25               | 119        |
| Chitosan/cellulose  | Cr(VI)  | 13.05                            | 25               | 119        |
| Chitosan/cellulose  | Ni(II)  | 13.21                            | 25               | 119        |
| Chitosan/cellulose  | Pb(II)  | 26.31                            | 25               | 119        |
| Chitosan/perlite  | Cu(II)  | 196.07                           | –                | 120        |
| Chitosan/perlite  | Ni(II)  | 114.94                           | –                | 120        |
| Chitosan/perlite  | Cd(II)  | 178.6                            | 25               | 121        |
| Chitosan/perlite  | Cr(VI)  | 153.8                            | 25               | 122        |
| Chitosan/perlite  | Cu(II)  | 104.0                            | 25               | 123        |
| Chitosan/ceramic alumina                                    | As(III) | 56.50                            | 25               | 124        |
| Chitosan/ceramic alumina                                    | As(V)   | 96.46                            | 25               | 124        |
| Chitosan/ceramic alumina                                    | Cu(II)  | 86.20                            | 25               | 125        |
| Chitosan/ceramic alumina                                    | Ni(II)  | 78.10                            | 25               | 125        |
| Chitosan/ceramic alumina                                    | Cr(VI)  | 153.8                            | 25               | 126        |
| Chitosan/montmorillonite                                    | Cr(VI)  | 41.67                            | 25               | 127        |
| Chitosan/alginate   | Cu(II)  | 67.66                            | –                | 128        |
| Chitosan/calcium alginate                                   | Ni(II)  | 222.2                            | –                | 129        |
| Chitosan/silica   | Ni(II)  | 254.3                            | –                | 129        |
| Chitosan/PVC  | Cu(II)  | 87.9                             | –                | 130        |
| Chitosan/PVC  | Ni(II)  | 120.5                            | –                | 130        |
| Chitosan/PVA  | Cd(II)  | 142.9                            | 50               | 131        |
| Chitosan/PVA  | Cu(II)  | 47.85                            | –                | 132        |
| Chitosan/sand   | Cu(II)  | 10.87                            | –                | 133        |
| Chitosan/sand   | Cu(II)  | 8.18                             | –                | 134        |
| Chitosan/sand   | Pb(II)  | 12.32                            | –                | 134        |
| Chitosan/clinoptilolite                                     | Cu(II)  | 574.49                           | –                | 135        |
| Chitosan/clinoptilolite                                     | Cu(II)  | 719.39                           | 25               | 136        |
| Chitosan/clinoptilolite                                     | Co(II)  | 467.90                           | 25               | 136        |
| Chitosan/clinoptilolite                                     | Ni(II)  | 247.03                           | 25               | 136        |
| Chitosan/nano-hydroxyapatite                                | Fe(III) | 6.75                             | –                | 137        |
| Poly(methacrylic acid) grafted-chitosan/bentonite           | Th(IV)  | 110.5                            | 30               | 138        |
| Chitosan-coated acid-treated oil palm shell charcoal (CCAB) | Cr(VI)  | 60.25                            | –                | 139        |
| Chitosan-coated oil palm shell charcoal (CCB)               | Cr(VI)  | 52.68                            | –                | 139        |
| Acid-treated oil palm shell charcoal (AOPSC)                | Cr(VI)  | 44.68                            | –                | 139        |

<sup>a</sup> These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions.

<sup>b</sup> In mg/g.

**TABLE 5.14**  
**Adsorption Capacities of Metals by Untreated and Pretreated Algae-Based Materials<sup>a</sup>**

| Algae  | Metals | Adsorption Capacity <sup>b</sup> | References |
|--|--------|----------------------------------|------------|
| <i>Ascophyllum nodosum</i> (B)   | Cd(II) | 0.338–1.913                      | 143        |
| <i>Ascophyllum nodosum</i>   | Ni(II) | 1.346–2.316                      | 144        |
| <i>Ascophyllum nodosum</i>   | Pb(II) | 1.313–2.307                      | 144        |
| <i>Ascophyllum nodosum</i> -CaCl <sub>2</sub> treated                                    | Cd(II) | 0.930                            | 145        |
| <i>Ascophyllum nodosum</i> -CaCl <sub>2</sub> treated                                    | Cu(II) | 1.090                            | 145        |
| <i>Ascophyllum nodosum</i> -CaCl <sub>2</sub> treated                                    | Pb(II) | 1.150                            | 145        |
| <i>Ascophyllum nodosum</i> -Bis(ethenil)sulfone treated                                  | Pb(II) | 1.733                            | 144        |
| <i>Ascophyllum nodosum</i> -divinil sulfone treated                                      | Cd(II) | 1.139                            | 143        |
| <i>Ascophyllum nodosum</i> -formaldehyde treated   | Cd(II) | 0.750                            | 146        |
| <i>Ascophyllum nodosum</i> -formaldehyde treated   | Cd(II) | 0.750                            | 147        |
| <i>Ascophyllum nodosum</i> -formaldehyde treated   | Cd(II) | 0.854                            | 147        |
| <i>Ascophyllum nodosum</i> -formaldehyde treated   | Cu(II) | 0.990                            | 146        |
| <i>Ascophyllum nodosum</i> -formaldehyde treated   | Cu(II) | 1.306                            | 147        |
| <i>Ascophyllum nodosum</i> -formaldehyde treated   | Cu(II) | 1.432                            | 147        |
| <i>Ascophyllum nodosum</i> -formaldehyde treated   | Pb(II) | 1.3755                           | 147        |
| <i>Ascophyllum nodosum</i> -formaldehyde treated   | Ni(II) | 1.618                            | 147        |
| <i>Ascophyllum nodosum</i> -formaldehyde treated   | Ni(II) | 1.431                            | 147        |
| <i>Ascophyllum nodosum</i> -formaldehyde treated   | Zn(II) | 0.680                            | 146        |
| <i>Ascophyllum nodosum</i> -formaldehyde treated   | Zn(II) | 0.719                            | 147        |
| <i>Ascophyllum nodosum</i> -formaldehyde treated   | Zn(II) | 0.8718                           | 147        |
| <i>Ascophyllum nodosum</i> -formaldehyde (3CdSO <sub>4</sub> , H <sub>2</sub> O) treated | Cd(II) | 1.121                            | 143        |
| <i>Ascophyllum nodosum</i> -formaldehyde + CH <sub>3</sub> COOH treated                  | Ni(II) | 0.409                            | 144        |
| <i>Ascophyllum nodosum</i> -formaldehyde + CH <sub>3</sub> COOH treated                  | Pb(II) | 1.308                            | 144        |
| <i>Ascophyllum nodosum</i> -formaldehyde + urea treated                                  | Cd(II) | 1.041                            | 143        |
| <i>Ascophyllum nodosum</i> -formaldehyde + urea treated                                  | Ni(II) | 0.511                            | 144        |
| <i>Ascophyllum nodosum</i> -formaldehyde + urea treated                                  | Pb(II) | 0.854                            | 144        |
| <i>Ascophyllum nodosum</i> -formaldehyde Cd(CH <sub>3</sub> COO) <sub>2</sub> treated    | Cd(II) | 1.326                            | 143        |
| <i>Ascophyllum nodosum</i> -glutaraldehyde treated                                       | Cd(II) | 1.259                            | 143        |
| <i>Ascophyllum nodosum</i> -glutaraldehyde treated                                       | Cd(II) | 0.480                            | 147        |
| <i>Ascophyllum nodosum</i> -glutaraldehyde treated                                       | Cd(II) | 0.4626                           | 147        |
| <i>Ascophyllum nodosum</i> -glutaraldehyde treated                                       | Cu(II) | 0.8497                           | 147        |
| <i>Ascophyllum nodosum</i> -glutaraldehyde treated                                       | Cu(II) | 0.803                            | 147        |
| <i>Ascophyllum nodosum</i> -glutaraldehyde treated                                       | Ni(II) | 0.9199                           | 147        |
| <i>Ascophyllum nodosum</i> -glutaraldehyde treated                                       | Ni(II) | 1.959                            | 147        |
| <i>Ascophyllum nodosum</i> -glutaraldehyde treated                                       | Pb(II) | 1.318                            | 144        |
| <i>Ascophyllum nodosum</i> -glutaraldehyde treated                                       | Pb(II) | 0.898                            | 147        |
| <i>Ascophyllum nodosum</i> -glutaraldehyde treated                                       | Pb(II) | 0.8157                           | 147        |
| <i>Ascophyllum nodosum</i> -glutaraldehyde treated                                       | Zn(II) | 0.3671                           | 147        |
| <i>Ascophyllum nodosum</i> -glutaraldehyde treated                                       | Zn(II) | 0.138                            | 147        |
| <i>Caulerpa lentillifera</i> (G)-dried macroalgae  | Cu(II) | 0.042–0.088                      | 148        |
| <i>Caulerpa lentillifera</i> (G)-dried macroalgae  | Cd(II) | 0.026–0.042                      | 148        |
| <i>Caulerpa lentillifera</i> (G)-dried macroalgae  | Pb(II) | 0.076–0.139                      | 148        |
| <i>Caulerpa lentillifera</i> (G)-dried macroalgae  | Zn(II) | 0.021–0.141                      | 148        |
| <i>Caulerpa lentillifera</i> (G)-dried macroalgae  | Cu(II) | 0.112                            | 149        |
| <i>Caulerpa lentillifera</i> (G)-dried macroalgae  | Cd(II) | 0.0381                           | 149        |
| <i>Caulerpa lentillifera</i> (G)-dried macroalgae  | Pb(II) | 0.142                            | 149        |
| <i>Chaetomorpha linum</i> (G)  | Cd(II) | 0.48                             | 150        |
| <i>Chlorella miniata</i> (G)   | Cu(II) | 0.366                            | 151        |

(Continued)



TABLE 5.14 (Continued)

Adsorption Capacities of Metals by Untreated and Pretreated Algae-Based Materials<sup>a</sup>

| Algae  | Metals  | Adsorption Capacity <sup>b</sup> | References |
|--|---------|----------------------------------|------------|
| <i>Chlorella miniata</i>                                       | Ni(II)  | 0.237                            | 151        |
| <i>Chlorella vulgaris</i> (G)                                  | Cd(II)  | 0.30                             | 152        |
| <i>Chlorella vulgaris</i>                                      | Ni(II)  | 0.205–1.017                      | 152        |
| <i>Chlorella vulgaris</i>                                      | Pb(II)  | 0.47                             | 152        |
| <i>Chlorella vulgaris</i>                                      | Zn(II)  | 0.37                             | 152        |
| <i>Chlorella vulgaris</i>                                      | Cr(VI)  | 0.534                            | 153        |
| <i>Chlorella vulgaris</i>                                      | Cr(VI)  | 1.525                            | 154        |
| <i>Chlorella vulgaris</i>                                      | Cu(II)  | 0.295                            | 151        |
| <i>Chlorella vulgaris</i>                                      | Cu(II)  | 0.254–0.549                      | 153        |
| <i>Chlorella vulgaris</i>                                      | Cu(II)  | 0.758                            | 154        |
| <i>Chlorella vulgaris</i>                                      | Fe(III) | 0.439                            | 153        |
| <i>Chlorella vulgaris</i>                                      | Ni(II)  | 1.017                            | 154        |
| <i>Chlorella vulgaris</i>                                      | Ni(II)  | 0.205                            | 151        |
| <i>Chlorella vulgaris</i> -artificial cultivation              | Cr(IV)  | 1.525                            | 154        |
| <i>Chlorella vulgaris</i> -artificial cultivation              | Cu(II)  | 0.759                            | 154        |
| <i>Chlorella vulgaris</i> -artificial cultivation              | Ni(II)  | 1.017                            | 154        |
| <i>Cladophora glomerata</i> (G)                                | Pb(II)  | 0.355                            | 155        |
| <i>Chondrus crispus</i> (R)                                    | Ni(II)  | 0.443                            | 144        |
| <i>Chondrus crispus</i> treated with 1-chloro-2,3-epoxypropane | Pb(II)  | 1.009                            | 144        |
| <i>Chondrus crispus</i>  | Pb(II)  | 0.941                            | 144        |
| <i>Codium fragile</i> (G)                                      | Cd(II)  | 0.0827                           | 156        |
| <i>Codium taylori</i> (G)                                      | Ni(II)  | 0.099                            | 144        |
| <i>Codium taylori</i>  | Pb(II)  | 1.815                            | 144        |
| <i>Corallina officinalis</i> (R)                               | Cd(II)  | 0.2642                           | 156        |
| <i>Durvillaea potatorum</i> (B)-CaCl <sub>2</sub> treated      | Cd(II)  | 0.260                            | 157        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Cd(II)  | 1.130                            | 157        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Cd(II)  | 1.100                            | 157        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Cd(II)  | 1.100                            | 157        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Cd(II)  | 1.120                            | 157        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Cu(II)  | 0.940                            | 158        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Cu(II)  | 0.180                            | 158        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Cu(II)  | 0.990                            | 158        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Cu(II)  | 1.210                            | 158        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Cu(II)  | 1.310                            | 158        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Ni(II)  | 0.17                             | 159        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Ni(II)  | 0.68                             | 159        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Ni(II)  | 1.13                             | 159        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Pb(II)  | 0.020                            | 158        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Pb(II)  | 0.760                            | 158        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Pb(II)  | 1.290                            | 158        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Pb(II)  | 1.470                            | 158        |
| <i>Durvillaea potatorum</i> -CaCl <sub>2</sub> treated         | Pb(II)  | 1.550                            | 158        |
| <i>Ecklonia maxima</i> (B)-CaCl <sub>2</sub> treated           | Cd(II)  | 1.150                            | 145        |
| <i>Ecklonia maxima</i> -CaCl <sub>2</sub> treated              | Cu(II)  | 1.220                            | 145        |
| <i>Ecklonia maxima</i> -CaCl <sub>2</sub> treated              | Pb(II)  | 1.400                            | 145        |
| <i>Ecklonia radiata</i> (B)-CaCl <sub>2</sub> treated          | Cd(II)  | 1.040                            | 145        |
| <i>Ecklonia radiata</i> -CaCl <sub>2</sub> treated             | Cu(II)  | 0.070                            | 158        |
| <i>Ecklonia radiata</i> -CaCl <sub>2</sub> treated             | Cu(II)  | 0.450                            | 158        |

(Continued)

TABLE 5.14 (Continued)

Adsorption Capacities of Metals by Untreated and Pretreated Algae-Based Materials<sup>a</sup>

| Algae  | Metals | Adsorption Capacity <sup>b</sup> | References |
|--|--------|----------------------------------|------------|
| <i>Ecklonia radiata</i> -CaCl <sub>2</sub> treated       | Cu(II) | 0.950                            | 158        |
| <i>Ecklonia radiata</i> -CaCl <sub>2</sub> treated       | Cu(II) | 1.060                            | 158        |
| <i>Ecklonia radiata</i> -CaCl <sub>2</sub> treated       | Cu(II) | 1.110                            | 158        |
| <i>Ecklonia radiata</i> -CaCl <sub>2</sub> treated       | Pb(II) | 0.050                            | 158        |
| <i>Ecklonia radiata</i> -CaCl <sub>2</sub> treated       | Pb(II) | 0.420                            | 158        |
| <i>Ecklonia radiata</i> -CaCl <sub>2</sub> treated       | Pb(II) | 0.990                            | 158        |
| <i>Ecklonia radiata</i> -CaCl <sub>2</sub> treated       | Pb(II) | 1.170                            | 158        |
| <i>Ecklonia radiata</i> -CaCl <sub>2</sub> treated       | Pb(II) | 1.260                            | 158        |
| <i>Fucus vesiculosus</i> (B)                             | Cd(II) | 0.649                            | 143        |
| <i>Fucus vesiculosus</i>                                 | Ni(II) | 0.392                            | 144        |
| <i>Fucus vesiculosus</i>                                 | Pb(II) | 1.105–2.896                      | 144        |
| <i>Fucus vesiculosus</i> -formaldehyde treated           | Ni(II) | 0.559                            | 144        |
| <i>Fucus vesiculosus</i> -formaldehyde treated           | Pb(II) | 1.752                            | 144        |
| <i>Fucus vesiculosus</i> -formaldehyde + HCl treated     | Pb(II) | 1.453                            | 144        |
| <i>Galaxaura marginata</i> (R)                           | Ni(II) | 0.187                            | 144        |
| <i>Galaxaura marginata</i>                               | Pb(II) | 0.121                            | 144        |
| <i>Galaxaura marginata</i> -CaCO <sub>3</sub> treated    | Ni(II) | 0.187                            | 144        |
| <i>Galaxaura marginata</i> -CaCO <sub>3</sub> treated    | Pb(II) | 1.530                            | 144        |
| <i>Gracilaria corticata</i> (R)                          | Pb(II) | 0.2017–0.2606                    | 155        |
| <i>Gracilaria edulis</i> (R)                             | Cd(II) | 0.24                             | 150        |
| <i>Gracilaria salicornia</i> (R)                         | Cd(II) | 0.16                             | 150        |
| <i>Laminaria hyperbola</i> (B)-treated CaCl <sub>2</sub> | Cd(II) | 0.820                            | 145        |
| <i>Laminaria hyperbola</i> -treated CaCl <sub>2</sub>    | Cu(II) | 1.220                            | 145        |
| <i>Laminaria hyperbola</i> -treated CaCl <sub>2</sub>    | Pb(II) | 1.350                            | 145        |
| <i>Laminaria japonica</i> (B)-treated CaCl <sub>2</sub>  | Cd(II) | 1.110                            | 145        |
| <i>Laminaria japonica</i> -treated CaCl <sub>2</sub>     | Cu(II) | 1.200                            | 145        |
| <i>Laminaria japonica</i> -treated CaCl <sub>2</sub>     | Pb(II) | 1.330                            | 145        |
| <i>Lessonia flavicans</i> (B)-treated CaCl <sub>2</sub>  | Cd(II) | 1.160                            | 145        |
| <i>Lessonia flavicans</i> -treated CaCl <sub>2</sub>     | Cu(II) | 1.250                            | 145        |
| <i>Lessonia flavicans</i> -treated CaCl <sub>2</sub>     | Pb(II) | 1.450                            | 145        |
| <i>Lessonia nigrescens</i> (B)-treated CaCl <sub>2</sub> | Cd(II) | 1.110                            | 145        |
| <i>Lessonia nigrescens</i> -treated CaCl <sub>2</sub>    | Cu(II) | 1.260                            | 145        |
| <i>Lessonia nigrescens</i> -treated CaCl <sub>2</sub>    | Pb(II) | 1.460                            | 145        |
| <i>Padina</i> sp. (B)                                    | Cd(II) | 0.53                             | 160        |
| <i>Padina</i> sp.-CaCl <sub>2</sub> treated              | Cd(II) | 0.52                             | 160        |
| <i>Padina</i> sp.-CaCl <sub>2</sub> treated              | Cu(II) | 0.8                              | 161        |
| <i>Padina gymnospora</i> (B)                             | Ni(II) | 0.170                            | 144        |
| <i>Padina gymnospora</i>                                 | Pb(II) | 0.314                            | 144        |
| <i>Padina gymnospora</i> -CaCO <sub>3</sub> treated      | Ni(II) | 0.238                            | 144        |
| <i>Padina gymnospora</i> -CaCO <sub>3</sub> treated      | Pb(II) | 0.150                            | 144        |
| <i>Padina tetrastromatica</i> (B)                        | Pb(II) | 1.049                            | 155        |
| <i>Padina tetrastromatica</i>                            | Cd(II) | 0.53                             | 150        |
| <i>Polysiphonia violacea</i> (R)                         | Pb(II) | 0.4923                           | 155        |
| <i>Porphyra columbina</i> (R)                            | Cd(II) | 0.4048                           | 156        |
| <i>Sargassum</i> sp. (B)                                 | Cd(II) | 1.40                             | 162        |
| <i>Sargassum</i> sp.                                     | Cr(VI) | 1.3257                           | 163        |
| <i>Sargassum</i> sp.                                     | Cr(VI) | 1.30                             | 164        |
| <i>Sargassum</i> sp.                                     | Cu(II) | 1.08                             | 164        |

(Continued)

**TABLE 5.14 (Continued)**  
**Adsorption Capacities of Metals by Untreated and Pretreated Algae-Based Materials<sup>a</sup>**

| Algae   | Metals  | Adsorption Capacity <sup>b</sup> | References |
|---|---------|----------------------------------|------------|
| <i>Sargassum baccularia</i> (B)                       | Cd(II)  | 0.74                             | 150        |
| <i>Sargassum fluitans</i> (B)                         | Ni(II)  | 0.409                            | 144        |
| <i>Sargassum fluitans</i>                             | Pb(II)  | 1.594                            | 144        |
| <i>Sargassum fluitans</i> -epichlorohydrin treated    | Pb(II)  | 0.975                            | 144        |
| <i>Sargassum fluitans</i> -epichlorohydrin treated    | Ni(II)  | 0.337                            | 144        |
| <i>Sargassum fluitans</i> -formaldehyde treated       | Cd(II)  | 0.9519                           | 147        |
| <i>Sargassum fluitans</i> -formaldehyde treated       | Cu(II)  | 1.7938                           | 147        |
| <i>Sargassum fluitans</i> -formaldehyde treated       | Ni(II)  | 1.9932                           | 147        |
| <i>Sargassum fluitans</i> -formaldehyde treated       | Pb(II)  | 1.8244                           | 147        |
| <i>Sargassum fluitans</i> -formaldehyde treated       | Zn(II)  | 0.9635                           | 147        |
| <i>Sargassum fluitans</i> -formaldehyde + HCl treated | Ni(II)  | 0.749                            | 144        |
| <i>Sargassum fluitans</i> -glutaraldehyde treated     | Cd(II)  | 1.0676                           | 147        |
| <i>Sargassum fluitans</i> -glutaraldehyde treated     | Cu(II)  | 1.574                            | 147        |
| <i>Sargassum fluitans</i> -glutaraldehyde treated     | Ni(II)  | 0.7337                           | 147        |
| <i>Sargassum fluitans</i> -glutaraldehyde treated     | Pb(II)  | 1.6603                           | 147        |
| <i>Sargassum fluitans</i> -glutaraldehyde treated     | Zn(II)  | 0.9942                           | 147        |
| <i>Sargassum fluitans</i> -NaOH treated               | Al(III) | 0.950                            | 165        |
| <i>Sargassum fluitans</i> -NaOH treated               | Al(III) | 1.580                            | 165        |
| <i>Sargassum fluitans</i> -NaOH treated               | Al(III) | 3.740                            | 165        |
| <i>Sargassum fluitans</i> -NaOH treated               | Cu(II)  | 0.650                            | 165        |
| <i>Sargassum fluitans</i> -NaOH treated               | Cu(II)  | 1.350                            | 165        |
| <i>Sargassum fluitans</i> -NaOH treated               | Cu(II)  | 1.540                            | 165        |
| <i>Sargassum fluitans</i> -protonated biomass         | Cu(II)  | 0.710                            | 166        |
| <i>Sargassum fluitans</i> -protonated biomass         | Cu(II)  | 0.800                            | 166        |
| <i>Sargassum hystrix</i> (B)                          | Pb(II)  | 1.3755                           | 155        |
| <i>Sargassum natans</i> (B)                           | Cd(II)  | 1.174                            | 143        |
| <i>Sargassum natans</i>                               | Ni(II)  | 0.409                            | 144        |
| <i>Sargassum natans</i>                               | Pb(II)  | 1.221                            | 144        |
| <i>Sargassum natans</i>                               | Pb(II)  | 1.487                            | 155        |
| <i>Sargassum siliquosum</i> (M)                       | Cd(II)  | 0.73                             | 150        |
| <i>Sargassum vulgare</i> (M)                          | Ni(II)  | 0.085                            | 144        |
| <i>Sargassum vulgare</i>                              | Pb(II)  | 1.100                            | 144        |
| <i>Sargassum vulgare</i> -protonated biomass          | Cd(II)  | 0.790                            | 166        |
| <i>Sargassum vulgare</i> -protonated biomass          | Cu(II)  | 0.930                            | 166        |
| <i>Scenedesmus obliquus</i> (G)                       | Cu(II)  | 0.524                            | 154        |
| <i>Scenedesmus obliquus</i>                           | Ni(II)  | 0.5145                           | 154        |
| <i>Scenedesmus obliquus</i>                           | Cr(VI)  | 1.131                            | 154        |
| <i>Scenedesmus obliquus</i> -artificial cultivation   | Cr(VI)  | 1.131                            | 154        |
| <i>Scenedesmus obliquus</i> -artificial cultivation   | Cu(II)  | 0.524                            | 154        |
| <i>Scenedesmus obliquus</i> -artificial cultivation   | Ni(II)  | 0.514                            | 154        |
| <i>Ulva lactuca</i> (G)                               | Pb(II)  | 0.61                             | 155        |
| <i>Undaria pinnatifida</i> (B)                        | Pb(II)  | 1.945                            | 167        |

Note: (B): brown alga; (G): green alga; and (R): red alga.

<sup>a</sup> These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions.

<sup>b</sup> In mmol/g.

**TABLE 5.15**  
**Adsorption Capacities of Metals by Bacterials<sup>a</sup>**

| Metals                           | Adsorbent                         | Adsorption Capacity <sup>b</sup> | References |
|----------------------------------|-----------------------------------|----------------------------------|------------|
| Cd(II)                           | <i>Aeromonas caviae</i>           | 155.3                            | 169        |
|                                  | <i>Enterobacter</i> sp.           | 46.2                             | 170        |
|                                  | <i>Ochrobactrum anthropi</i>      | –                                | 171        |
|                                  | <i>Pseudomonas aeruginosa</i>     | 42.4                             | 172        |
|                                  | <i>Pseudomonas putida</i>         | 8.0                              | 173        |
|                                  | <i>Pseudomonas putida</i>         | 500.00                           | 174        |
|                                  | <i>Pseudomonas</i> sp.            | 278.0                            | 175        |
|                                  | <i>Sphingomonas paucimobilis</i>  | –                                | 176        |
|                                  | <i>Staphylococcus xylosus</i>     | 250.0                            | 175        |
|                                  | <i>Streptomyces pimprina</i>      | 30.4                             | 177        |
|                                  | <i>Streptomyces rimosus</i>       | 64.9                             | 178        |
| Cr(VI)                           | <i>Aeromonas caviae</i>           | 284.4                            | 169        |
|                                  | <i>Bacillus coagulans</i>         | 39.9                             | 179        |
|                                  | <i>Bacillus megaterium</i>        | 30.7                             | 179        |
|                                  | <i>Bacillus coagulans</i>         | 39.9                             | 179        |
|                                  | <i>Bacillus thuringiensis</i>     | 69.4                             | 180        |
|                                  | <i>Bacillus megaterium</i>        | 30.7                             | 179        |
|                                  | <i>Bacillus thuringiensis</i>     | 83.3                             | 181        |
|                                  | <i>Pseudomonas</i> sp.            | 95.0                             | 175        |
|                                  | <i>Pseudomonas fluorescens</i>    | 111.11                           | 174        |
|                                  | <i>Staphylococcus xylosus</i>     | 143.0                            | 175        |
|                                  | <i>Zoogloea ramigera</i>          | 2                                | 182        |
| Cu(II)                           | <i>Bacillus firmus</i>            | 381                              | 183        |
|                                  | <i>Bacillus</i> sp.               | 16.3                             | 184        |
|                                  | <i>Bacillus subtilis</i>          | 20.8                             | 185        |
|                                  | <i>Enterobacter</i> sp.           | 32.5                             | 170        |
|                                  | <i>Micrococcus luteus</i>         | 33.5                             | 185        |
|                                  | <i>Pseudomonas aeruginosa</i>     | 23.1                             | 172        |
|                                  | <i>Pseudomonas cepacia</i>        | 65.3                             | 186        |
|                                  | <i>Pseudomonas putida</i>         | 6.6                              | 173        |
|                                  | <i>Pseudomonas putida</i>         | 96.9                             | 187        |
|                                  | <i>Pseudomonas putida</i>         | 15.8                             | 188        |
|                                  | <i>Pseudomonas putida</i>         | 163.93                           | 174        |
|                                  | <i>Pseudomonas stutzeri</i>       | 22.9                             | 185        |
|                                  | <i>Sphaerotilus natans</i>        | 60                               | 189        |
|                                  | <i>Sphaerotilus natans</i>        | 5.4                              | 189        |
|                                  | <i>Streptomyces coelicolor</i>    | 66.7                             | 190        |
| <i>Thiobacillus ferrooxidans</i> | 39.8                              | 191                              |            |
| Fe(III)                          | <i>Streptomyces rimosus</i>       | 122.0                            | 192        |
| Ni(II)                           | <i>Bacillus thuringiensis</i>     | 45.9                             | 193        |
|                                  | <i>Pseudomonas putida</i>         | 556                              | 174        |
| Pb(II)                           | <i>Streptomyces rimosus</i>       | 32.6                             | 194        |
|                                  | <i>Bacillus</i> sp.               | 92.3                             | 184        |
|                                  | <i>Bacillus firmus</i>            | 467                              | 183        |
|                                  | <i>Corynebacterium glutamicum</i> | 567.7                            | 195        |
|                                  | <i>Enterobacter</i> sp.           | 50.9                             | 170        |

(Continued)

**TABLE 5.15 (Continued)**  
**Adsorption Capacities of Metals by Bacterials<sup>a</sup>**

| Metals | Adsorbent                              | Adsorption Capacity <sup>b</sup> | References |
|--------|--|----------------------------------|------------|
|        | <i>Pseudomonas aeruginosa</i>          | 79.5                             | 172        |
|        | <i>Pseudomonas aeruginosa</i>          | 0.7                              | 196        |
|        | <i>Pseudomonas putida</i>              | 270.4                            | 187        |
|        | <i>Pseudomonas putida</i>              | 56.2                             | 173        |
|        | <i>Streptomyces rimosus</i>            | 135.0                            | 197        |
| Pd(II) | <i>Desulfovibrio desulfuricans</i>     | 128.2                            | 198        |
|        | <i>Desulfovibrio fructosivorans</i>    | 119.8                            | 198        |
|        | <i>Desulfovibrio vulgaris</i>          | 106.3                            | 198        |
| Pt(IV) | <i>Desulfovibrio desulfuricans</i>     | 62.5                             | 198        |
|        | <i>Desulfovibrio fructosivorans</i>    | 32.3                             | 198        |
|        | <i>Desulfovibrio vulgaris</i>          | 40.1                             | 198        |
| Th(IV) | <i>Arthrobacter nicotianae</i>         | 75.9                             | 199        |
|        | <i>Bacillus licheniformis</i>          | 66.1                             | 199        |
|        | <i>Bacillus megaterium</i>             | 74.0                             | 199        |
|        | <i>Bacillus subtilis</i>               | 71.9                             | 199        |
|        | <i>Corynebacterium equi</i>            | 46.9                             | 199        |
|        | <i>Corynebacterium glutamicum</i>      | 36.2                             | 199        |
|        | <i>Micrococcus luteus</i>              | 77.0                             | 199        |
|        | <i>Zoogloea ramigera</i>               | 67.8                             | 199        |
| U(VI)  | <i>Arthrobacter nicotianae</i>         | 68.8                             | 199        |
|        | <i>Bacillus licheniformis</i>          | 45.9                             | 199        |
|        | <i>Bacillus megaterium</i>             | 37.8                             | 199        |
|        | <i>Bacillus subtilis</i>               | 52.4                             | 199        |
|        | <i>Corynebacterium equi</i>            | 21.4                             | 199        |
|        | <i>Corynebacterium glutamicum</i>      | 5.9                              | 199        |
|        | <i>Micrococcus luteus</i>              | 38.8                             | 199        |
|        | <i>Nocardia erythropolis</i>           | 51.2                             | 199        |
|        | <i>Zoogloea ramigera</i>               | 49.7                             | 199        |
| Zn(II) | <i>Streptomyces rimosus</i>            | 30                               | 200        |
|        | <i>Bacillus firmus</i>                 | 418                              | 183        |
|        | <i>Aphanothece halophytica</i>         | 133.0                            | 201        |
|        | <i>Pseudomonas putida</i>              | 6.9                              | 173        |
|        | <i>Pseudomonas putida</i>              | 17.7                             | 188        |
|        | <i>Streptomyces rimosus</i>            | 30.0                             | 200        |
|        | <i>Streptomyces rimosus</i>            | 80.0                             | 200        |
|        | <i>Streptoverticillium cinnamomeum</i> | 21.3                             | 202        |
|        | <i>Thiobacillus ferrooxidans</i>       | 82.6                             | 206        |
|        | <i>Thiobacillus ferrooxidans</i>       | 172.4                            | 191        |

<sup>a</sup> These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions.

<sup>b</sup> In mg/g.

production may vary with different rice species. Therefore, in many rice producing countries, the utilization of this abundant scaly residue is of great significance.

Rice husk is considered as a lignocellulosic agricultural byproduct that contains approximately 32.24% cellulose, 21.34% hemicelluloses, 21.44% lignin, and 15.05% mineral ash (59). The percentage of silica in its mineral ash is about 96.34% (60). Such a high percentage of silica coupled with

a large amount of lignin, a structural polymer, is very unusual in nature. It has made rice husk not only resistant to water penetration and fungal decomposition, but also resistant to the best efforts of man to dispose it since the rice husk does not biodegrade easily.

Of all cereal byproducts, rice husk has the lowest percentage of total digestible nutrients (<10%). It also contains very low protein and available carbohydrates, and yet, at the same time, high in crude fiber and crude ash. Owing to its abrasive character, poor nutritive value, low bulk density, and high ash content which would sometimes cause harmful effects, the husk is not widely used as animal feed.

Rice husk is a waste from a rice cultivation perspective. From an agricultural byproducts utilization perspective, however, rice husk is a resource yet to be fully utilized and exploited. The researchers are thus looking for ways to valorize rice husk. Efforts have been made to utilize rice husk as a building material. In this regard, rice husk is used to insulate walls, floors, and roof cavities because of its excellent properties, such as good heat insulation, does not emit smell or gases, and it is not corrosive. Unfortunately, the cost of building materials manufactured using rice husk as the aggregate is not competitive with that using other aggregates.

Thus, another interesting possibility for utilizing this cheap and readily available resource might be as a low-cost adsorbent in the removal of heavy metals from aqueous environment. The excellent characteristics of rice husk such as its insolubility in water, good chemical stability, high mechanical strength, and its granular structure, make this likelihood to be higher. Considerable researches have been attempted on the use of rice husk, either untreated or modified, to remove heavy metals using different methods. Adsorption capacities of metals by untreated and treated rice husk are presented in Table 5.11.

### 5.3.3 WHEAT STRAW AND WHEAT BRAN

Every year, large amounts of straw and bran from *Triticum aestivum* (wheat), a major food crop of the world, are produced as byproducts/waste materials. Wheat straw has been used as fodder and in paper industry to produce low-quality boards or packing materials. The stems are burnt directly in some parts of the world for energy purposes, adding seriously to atmospheric pollution and wastage of resources.

The main components found in wheat straw are cellulose (37%–39%), hemicellulose (30%–35%), lignin (~14%), and sugars. Considering its chemical properties, wheat straw normally consists of different functional groups such as carboxyl, hydroxyl, sulfhydryl, amide, amine, and so on. The percentage composition of different substances varies in different parts of the world, although the substances are almost similar.

Both wheat straw and wheat bran have been investigated for their adsorption behavior toward metal ions (Table 5.12). The reported variations in metal capacities of wheat-based materials correspond to the variation in the structure of wheat bran used in different studies, along with other parameters. Apart from this, the discrepancies in the origin, area, soil, and kind of wheat from where wheat-based material is obtained may explain such a variation in results.

### 5.3.4 CHITIN, CHITOSAN, AND CHITOSAN COMPOSITES

The utilization of byproducts, chitin, generated from crustacean processing could be helpful in addressing the environmental problem as the biodegradation of this waste is very slow in nature. As a matter of fact, the application of biopolymers such as chitin and chitosan can be seen as one of the emerging techniques for the removal of certain hazardous pollutants from the environment.

Chitin is the second most abundant polymer in nature after cellulose. It is a kind of natural biopolymer which has a chemical structure similar to cellulose and is generally found in a wide range of natural sources such as in the exoskeletons of crustaceans, cell wall of fungi, insects, annelids, and molluscs. It contains 2-acetamido-2-deoxy- $\beta$ -D-glucose through a  $\beta$  (1  $\rightarrow$  4) linkage. Chitosan

is a type of natural poly(aminosaccharide) consisting mainly of a poly(1 → 4)-2-amino-2-deoxy-D-glucose unit, synthesized from the deacetylation of chitin. Chitosan is known as an excellent biomaterial because of its special characteristics, for instance, hydrophilicity, biocompatibility, biodegradability, nontoxicity, and good adsorption properties.

Apart from the mentioned physicochemical characteristics, the possibility of using chitin in a variety of forms, from flake types to gels, beads, and fibers is also the contributing factor as to why this waste material has drawn particular attention. It has been demonstrated that chitin can provide readily available binding sites for a wide range of molecules due to its high contents of amino and hydroxyl functional groups. Nevertheless, the adsorption properties would still depend strongly on the sources of chitin, the degree of N-acetylation, and on variations in crystallinity and amino content.

Chitosan is very sensitive to pH as it can either form gel or dissolve depending on the pH values. Apparently, this characteristic has limited chitosan's performance as a biosorbent in wastewater treatment. To overcome this problem, cross-linking reagents such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycol diglycidyl ether, and isocyanates have been used to stabilize chitosan in acidic media. Cross-linking agents do not only prevent chitosan from becoming soluble under these conditions but also enhance its mechanical properties. As a result, cross-linked chitosan not only has stronger mechanical properties compared with its parent biopolymer, but might also have higher affinity for the targeted pollutants.

Biosorption using chitosan-based materials, such as chitosan derivatives and chitosan composites have been extensively investigated for the removal of heavy metals. Among them are chitosan derivatives containing nitrogen, phosphorus, and sulfur as heteroatoms, and other derivatives such as chitosan-crown ethers and chitosan-ethylenediaminetetraacetic acid (EDTA)/diethylenetriamine-pentaacetic acid (DTPA) complexes. As for chitosan composites, various kinds of substances have been used to form composites with chitosan, which include montmorillonite, polyurethane, activated clay, bentonite, polyvinyl alcohol, polyvinyl chloride, kaolinite, oil palm ash, and perlite. Table 5.13 presents the heavy metal removal capacities through adsorption process by chitosan and chitosan composites.

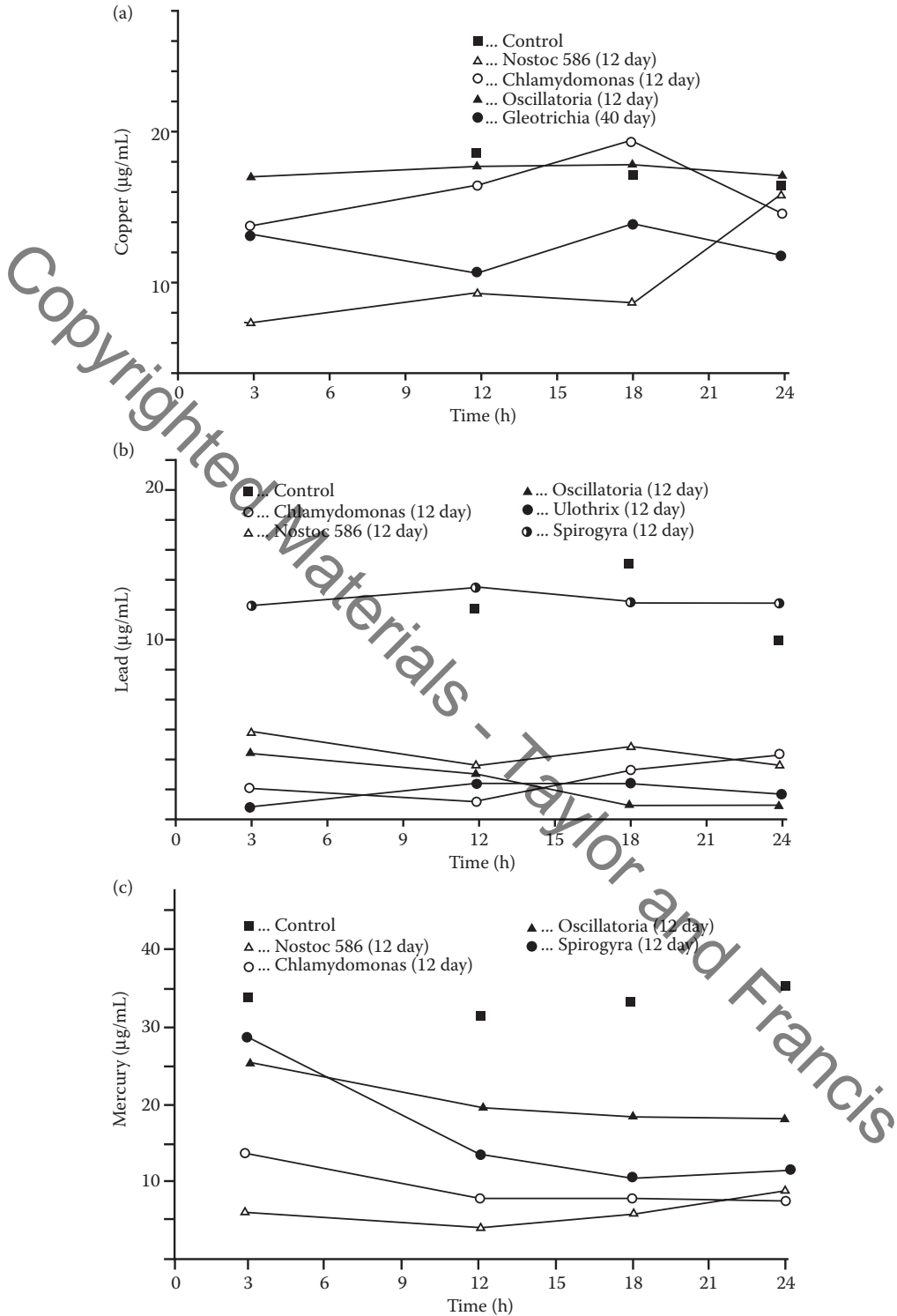
### 5.3.5 ALGAE

Algae are a large and diverse group of simple plant-like organisms, ranging from unicellular to multicellular forms, which can be seen in aquatic habitats, freshwater, marine, and moist soil. Algae contain chlorophyll and carry out oxygenic photosynthesis. This biosorbent has been extensively studied due to its ubiquitous occurrence in nature. Algae have found applications as fertilizer, energy sources, pollution control, stabilizing substances, in nutrition, etc. Figure 5.5 presents efficiency of heavy metals uptake by various algae.

Several characteristics are used to classify algae, including the nature of the chlorophyll(s) present, the carbon reserve polymers produced, the cell-wall structure, and the type of motility. Although all algae contain chlorophyll a, there are some, which contain other chlorophylls that differ in minor ways from chlorophylls a. The presence of these additional chlorophylls is characteristic of particular algal groups. The major groups of algae include Chrysophyta (golden-brown algae, diatoms), Euglenophyta (euglenoids is also considered as protozoa), Pyrrophyta (dino-flagellates), Chlorophyta (green algae), Phaeophyta (brown algae), and Rhodophyta (red algae). Adsorption capacities of metals by untreated and treated algae are provided in Table 5.14. From the published literatures, brown algae are the most widely studied among the three groups of algae (red, green, and brown algae). This could be related to sorption capability of the algae, whereby brown algae emerges to offer better sorption than red or green algae (141,142). Researchers have used mainly brown algae treated in different ways to improve their sorption capacity (141).

The algal cell is surrounded by a thin, rigid cell wall that contains pores of about 3–5 nm wide to allow low molecular-weight constituents such as water, ions, gases, and other nutrients to pass through freely for metabolism and growth. However, the cell walls are essentially impermeable to





**FIGURE 5.5** Uptake of heavy metals (a) Cu, (b) Pb, and (c) Hg by various algae. (From US Environmental Protection Agency. 1983. *Factors Influencing Metal Accumulation by Algae*, EPA-600/S2-82-100. US EPA, Cincinnati, OH.)

larger molecules or to macromolecules. It is usually made of a multilayered microfibrillar framework generally consisting of cellulose and interspersed with amorphous material (168).

In biosorption, various algae have been used and investigated for heavy metal removal in aqueous solutions by a number of researchers. The metal biosorption by algae mainly depend on the components on the cell, especially through cell surface and the spatial structure of the cell wall. Various functional groups, such as carboxyl, hydroxyl, sulfate, and amino groups in algal cell-wall polysaccharides have been proven to play a very important role in metal binding. The biomass characteristics, physicochemical properties of the targeted metals, and solution pH also have a significant impact on the biosorption performance.

### 5.3.6 BACTERIA

Bacteria are microscale organisms whose single cells have neither a membrane-bound nucleus nor other membrane-bound organelles such as the mitochondria and chloroplasts. They have simple morphology and commonly present in three basic shapes: spherical or ovoid (coccus), rod (bacillus, with a cylindrical shape), and spiral (spirillum). Bacteria vary in size as much as in shape due to differences in genetics and ecology. The smallest bacteria are about 0.3  $\mu\text{m}$ , and a few bacteria become fairly large, for example, some spirochetes occasionally reach 500  $\mu\text{m}$  in length, and cyanobacterium *Oscillatoria* is about 7  $\mu\text{m}$  in diameter.

A “typical” bacterial cell (e.g., *Escherichia coli*) contains cell wall, cell membrane, and cytoplasmic matrix consisting of several constituents, which are not membrane-enclosed: inclusion bodies, ribosomes, and the nucleoid with its genetic material. Some bacteria have special structure, such as flagella and S-layer. The major function of the cell wall is to (i) provide the cell shape and protect it from osmotic lysis, (ii) protect cell from toxic substances, and (iii) to offer the site of action for several antibiotics. Moreover, it is a necessary component for normal cell division. Cellular wall shape and strength are primarily due to peptidoglycan. The amount and exact composition of peptidoglycan are only found in cell walls and vary among the major bacterial groups.

Bacteria are of special interest in search for and the development of new biosorbent materials due to their availability, small size, ubiquity, ability to grow under controlled conditions, and resiliency to a wide range of environmental situations. Adsorption capacities of metals by bacterial surfaces are given in Table 5.15.

## 5.4 CHEMICAL PROPERTIES AND CHARACTERIZATION STUDIES

Fourier-transform infrared spectroscopy (FTIR) spectrum analysis is usually used to study the functional groups on the adsorbents. UV-Vis spectroscopy is used to investigate whether the removal of Cr(VI) involves the reduction of Cr(VI) to Cr(III) by measuring the absorbance of the purple-violet complex of Cr(VI) with 1,5-diphenylcarbazide acidic solution at 540 nm. The difference between the total and Cr(VI) concentrations was taken to represent the Cr(III) concentration.

To elucidate the surface morphology of the adsorbents before and after sorption, several techniques can be used which include scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). Both SEM and TEM involved the use of focused beam of electrons instead of light to “image” the materials of interest and gain information as to its structure and composition. Whereas for AFM, it is a stylus-type instrument, in which a sharp probe, scanned raster-fashion across the sample, is used to detect changes in the surface structure on the atomic scale. As the interaction force between the cantilever tip and surface varies, deflections are produced in the cantilever. These deflections are measured, and used to compile a topographic image of the surface. Color mapping is the usual method used for displaying the data where light color indicates high features or high topography and lower topography is shown by darker color. And often, if the adsorbents were subjected to chemical modifications, the resulting materials become more intense and display a higher topography.

## 5.5 INFLUENCE OF OPERATIONAL PARAMETERS

### 5.5.1 EFFECT OF pH

Since the efficiency of the adsorption process is strongly dependent on pH, in most of the adsorption process of heavy metals by various low-cost adsorbents, pH is one of the commonly examined parameters. Generally, the prominent effect of this parameter is because the solution pH influences the metal chemistry as well as the surface binding sites of the biosorbents. From the literature, it is evident that at certain pH, the metal ions could be precipitated out as hydroxides. Therefore, in most of the studies, the solution pH at which precipitation occurred will not be investigated since the dominant removal process was due to precipitation and not of experimental interest. In most of the lignocellulosic adsorbents, the presence of carboxyl functional groups has been well documented. It is suggested that at low pH (<2.0), the carboxyl groups on the surface of the adsorbents were predominantly protonated ( $-\text{COOH}$ ), and hence incapable of binding the cationic species. With increasing pH, adsorption became favorable as the adsorption sites were made available for binding positively charged metal ions.

In the adsorption of Cr(VI) using natural rice hull (NRH) and ethylenediamine-modified rice hull (enRH), the modified adsorbent exhibited greater uptake capability for Cr(VI) and the adsorption decreased with increasing pH (203). This is due to the distribution of Cr(VI) species which is controlled by the ion equilibria and the total Cr(VI) concentration used. Under the experimental condition, it is postulated that  $\text{HCrO}_4^-$  was the major species and played an important role in association with the adsorbents. At low pH, the amine groups on the surface of enRH was protonated by  $\text{H}^+$ , rendering it favorable for electrostatic attraction between  $\text{HCrO}_4^-$  and positively charged binding sites. The lower uptake at pH 1 is closely related to the reduction of Cr(VI) to Cr(III). It has been well documented that under acidic conditions, Cr(VI) demonstrates a very high positive redox potential which denotes it is strongly oxidizing and unstable in the presence of electron donors (204). The absence of lone pair in NRH as compared with those present in enRH explained the low reduction capability of NRH, and thereby, adsorption decreased with increasing pH.

Generally, an adsorption process is accompanied by a decrease in pH due to the release of  $\text{H}^+$ . However, exception cases were observed in the adsorption involving Cr(VI) and As(V). The increase in pH implies the release of  $\text{OH}^-$  ions into the solution upon protonation of the adsorbents.

### 5.5.2 EFFECT OF INITIAL CONCENTRATION OF HEAVY METALS AND CONTACT TIME

The nature of the adsorbent and its available binding sites played a crucial role in determining the time needed for the attainment of equilibrium. Nevertheless, the typical adsorption pattern exhibited by various adsorbents in adsorbing heavy metals is a rapid ion-exchange process followed by chemisorption. The fast initial metal uptake is attributed to the rapid attachment of heavy metals onto the surface of the adsorbents, whereas the following slower adsorption is related to the interior penetration (intraparticle diffusion). In terms of initial heavy metals concentrations, the trend of uptake usually followed the normal course of adsorption process; the least concentrated showing the highest percentage uptake while the amount of heavy metals adsorbed decreased. Adsorption process involving a mixture of heavy metals sometimes reached equilibrium faster than those metals that present singly. The faster adsorption rate in this kind of systems could be due to the higher total metal ion concentration in the system which in turn gives rise to a greater driving force and collision probability between metal ions and the adsorbent. By comparing the uptake of heavy metal ions that are present in a mixture or single metal ion solution showed that the effect could be synergistic or antagonistic. Different explanations have been given regarding the sorption affinity of the adsorbents and these include competitive effect, ionic size, stability of the bond between the metal ions and the adsorbents, nature of metal-ion sorbents, interaction, and the distribution of the reaction group on the adsorbents (205).

### 5.5.3 EFFECT OF THE CHELATOR

One of the common problems associated with heavy metals removal in the conventional treatment method is the presence of a chelator. The chelators could mask the presence of metal ions, rendering their removal from the solution difficult or impossible. Owing to this, the effect of chelators that are commonly found in the environment, such as ethylenediamine tetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and salicylic acid (SA) were often tested for their influence on the adsorption of heavy metals. NTA is chosen because it is a substitute used for polyphosphate in the detergent whereas SA is representing humic acid which is reported to be present in natural wastes. For the adsorption of Cu(II) and Pb(II), the results have shown that both NTA and EDTA inhibit the metals uptake by the modified adsorbent (79). This is because NTA and EDTA formed stable complexes with Cu(II) and Pb(II) and they compete more effectively with the binding sites of both metal ions. The effectiveness of a chelator is expressed in chelator stability constants,  $\log K_1$  where the larger  $\log K_1$  value will give higher efficiency of the chelating effect. The results obtained were in accordance with the  $\log K_1$  values of 5.55, 9.80, and 16.28, respectively. Therefore, it is of utmost important to assess critically and differently the adsorption of heavy metals by various adsorbents if chelators are known to be present in the same system because it could be a significant suppressing effect.

## 5.6 EXPERIMENTAL METHODS AND MODELING OF HEAVY METALS ADSORPTION

### 5.6.1 BATCH ADSORPTION EXPERIMENTS

In a batch adsorption experiment, the adsorbent must be in contact with the adsorbate for a period of time to ensure that the concentration of the adsorbate in solution is in equilibrium with the adsorbate on the surface. Usually, the time required for the attainment of equilibrium is pH, concentration, agitation and is particle size dependent. For the batch equilibrium operations, a porous adsorbent with a smaller particle size is generally favored for its higher surface area, resulting in a more effective adsorbent–adsorbate contact and in a reduction of diffusional resistance inside the pores. After the adsorption process, the solid (adsorbent and adsorbate absorbed) and liquid phases (adsorbate residue in solution) are separated via several methods, for example, settling, filtration, or centrifugation. Owing to the cost involved, the used adsorbent is either discarded or regenerated. The most common applicability of batch adsorption studies will be in adsorption isotherm and kinetics modeling.

### 5.6.2 EQUILIBRIUM MODELING OF BIOSORPTION IN A BATCH SYSTEM

The adsorption properties and equilibrium data are usually known as adsorption isotherms. They are considered as the basic, yet the key requirements in adsorption system design. The good enough description of the adsorbate–adsorbent interaction provided by these data can optimize the application of the adsorbents. Apart from establishing an appropriate and correct correlation for the equilibrium data, the compliance of the data to a suitable mathematical model is also equally important. An accurate mathematical description is crucial for a reliable prediction on the adsorption parameters. It is also essential to allow a quantitative comparison on the adsorption behavior of different adsorption systems under a variety operating conditions.

Adsorption equilibrium is achieved when the amount of adsorbate being adsorbed onto the adsorbent is equal to the amount being desorbed. The equilibrium condition can be represented by plotting the adsorbate concentration in solid phase versus that in liquid phase. The position of equilibrium in the adsorption process is measured from the distribution of adsorbate molecules between the adsorbent and the liquid phase, which can generally be expressed by one or more of a series of isotherm models. The shape generated from an isotherm is usually used to predict the “favorable” behavior of

an adsorption system. Besides, the isotherm shape provides qualitative information on the nature of the solute–surface interaction. The adsorption isotherms are also applied extensively in the determination of the maximum adsorption capacity of adsorbents for a particular adsorbate. This information is important as a fundamental and convenient tool to evaluate the performance of different adsorbents and select the most appropriate one for a particular adsorption application under certain conditions.

On the other hand, two- and three-parameter models, originally used for gas-phase adsorption, are available and readily adopted to correlate adsorption equilibria in liquid-phase adsorption. The experimental adsorption data are well described by the equilibrium isotherm equations generated from each model. The different equation parameters and the underlying thermodynamic assumptions of these models often provide insight into the adsorption mechanism, surface properties, and affinity of the adsorbent. Apparently, establishing the most appropriate correlation of equilibrium curves is crucial in optimizing the adsorption condition, subsequently contributing to an improvement of the adsorption system.

### 5.6.2.1 Two-Parameter Isotherms

Langmuir, Freundlich, and Brunauer–Emmet–Teller (BET) models are some of the widely met isotherms. Meanwhile, Dubinin–Radushkevich (D–R) and Temkin isotherms appear to be gaining less popularity among the two-parameter models. Other seldom used two-parameter models such as Halsey and Hurkins–Jura (H–J) are also discussed briefly. The application of each model for an adsorption system is often limited by assumptions made within the model.

#### 5.6.2.1.1 Langmuir Isotherm

The Langmuir model is one of most popular isotherm models used to quantifying the amount of the adsorbed adsorbate on an adsorbent as a function of concentration at a particular temperature (207). Inherent within this model, some assumptions are valid for a biosorption process, including monolayer coverage of the adsorbate over a homogeneous adsorbent surface. All the sites on the adsorbent are equivalent and once an adsorbate molecule occupies a site, no further adsorption can take place at that site. Therefore, this model assumes occurrence of adsorption takes place at specific homogeneous sites on the surface of the adsorbent. Graphically, a plateau in the plot of  $q_e$  versus  $C_e$  characterizes the Langmuir isotherm. This explains why no further adsorption is allowed at equilibrium where a saturation point is reached. In addition, the Langmuir equation is applicable to homogeneous adsorption where the adsorption of each molecule has equal adsorption activation energy. Thus, this isotherm model is always utilized to describe adsorption of an adsorbate molecule from a liquid solution as

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (5.1)$$

where

$q_{\max}$  = mass of the adsorbate adsorbed/mass of adsorbent for a complete monolayer

$K_L$  = Langmuir constant related to the enthalpy of adsorption

The Langmuir equation can be written in different linear forms as

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{K_L q_{\max}} \quad (5.2)$$

$$\frac{1}{q_e} = \left( \frac{1}{K_L q_{\max}} \right) \frac{1}{C_e} + \frac{1}{q_{\max}} \quad (5.3)$$

$$q_e = q_{\max} - \left( \frac{1}{K_L} \right) \frac{q_e}{C_e} \quad (5.4)$$

$$\frac{q_e}{C_e} = K_L q_{\max} - K_L q_e \quad (5.5)$$

In some cases, different isotherm parameters are obtained using the four Langmuir linear equations (Equations 5.2 through 5.5), but they are identical when the nonlinear method is applied. Hence, the nonlinear method exists as a better approach to obtain the isotherm parameters (208). Despite better result provided by the nonlinear method, the linear least-square method is still more favorable among the researchers due to its simplicity and convenience.

The Langmuir isotherm is considered as the conventional method used in quantifying the maximum uptake and estimating the adsorption capacity  $q_{\max}$  of different adsorbents. The obtained  $q_{\max}$  should logically be temperature independent as it is supposed to coincide with saturation of a fixed number of identical surface sites that possess equal affinity for the adsorbate. However, small to modest changes in adsorption capacity with temperature is usually detected in real experimental conditions. The divergence from its formulation strongly indicates the presence of the surface functional groups on the adsorbent rather than a set of identical surface sites that are related to the saturation limit. Practically, the adsorption capacity is always influenced by the number of active sites on the adsorbent, the chemical state of the sites, the affinity between the sites (i.e., binding strength), and by the sites accessible to the adsorbate.

The Langmuir adsorption model suffers from the disadvantage of failure to account for the surface roughness of the adsorbate. Availability of multiple site-type that has arisen from rough inhomogeneous surfaces and changing of some parameters from site to site, such as the heat of adsorption has made this model to deviate drastically in many cases. Other than that, adsorbate–adsorbent interactions are ignored in this model. It has been proven experimentally that the existence of adsorbate–adsorbent interactions in heat of adsorption data, namely direct interaction and indirect interaction must be taken into consideration. In direct interactions, the adjacent adsorbed molecules can make adsorbing near another adsorbate molecule more or less favorable. Meanwhile, indirect interaction is referred to as the tendency of the adsorbate to change the surface around the adsorbed site, subsequently affecting the adsorption behavior of the nearby sites.

The decrease of  $K_L$  value with elevating temperature is an indicator for the exothermic nature of the adsorption process (209–212). In a physical adsorption, the bonding between adsorbates and the surface was primarily by physical forces, which become weaken at higher temperatures. Meanwhile, the endothermic process of the binding of adsorbates to active sites needs thermal energy; thus the elevation in temperature was more favorable for chemisorption (endothermic) (213). Alternatively, the exothermic or endothermic nature of the adsorption process can be further confirmed using the van't Hoff plots. An integrated van't Hoff equation provides the thermodynamic property and it relates the Langmuir constant,  $K_L$  to the temperature as

$$K_L = K_0 \exp\left(-\frac{\Delta H}{RT}\right) \quad (5.6)$$

where

$K_0$  = parameter of the van't Hoff equation

$\Delta H$  = enthalpy of adsorption



### 5.6.2.1.2 Freundlich Isotherm

Freundlich isotherm (214) is another most frequently used isotherm for description of heterogeneous systems. In fact, this isotherm model is the oldest of the nonlinear isotherms. It assumes neither homogenous site energies nor limited levels of adsorption. Therefore, concentration of adsorbate on the adsorbent surface increases with increasing adsorbate concentration in the system. The exponential equation is expressed in following form:

$$q_e = K_F C_e^{1/n} \quad (5.7)$$

where

$q_e$  = mass of the adsorbate adsorbed/mass adsorbent

$C_e$  = adsorbate concentration in solution, mass/volume

$K_F$  = Freundlich constant related to adsorption capacity at a particular temperature

$n$  = Freundlich constant related to adsorption intensity at a particular temperature ( $n > 1$ )

Equation 5.1 can also be written in a linearized logarithmic form

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5.8)$$

By plotting  $\log q_e$  versus  $\log C_e$ , values of  $1/n$  and  $\log K_F$  can be obtained from the graph slope and intercept, respectively.  $\log K_F$  is equivalent to  $\log q_e$  when  $C_e$  equals unity. The  $K_F$  value depends on the units upon which  $q_e$  and  $C_e$  are expressed if  $1/n \neq 1$ . Usually, Freundlich constant  $n$  ranges from 1 to 10 for a favorable adsorption. Larger value of  $n$  may indicate a stronger interaction between the adsorbent and the adsorbate. On the contrary, linear adsorption leading to identical adsorption energies for all sites is observed when  $1/n$  equals 1 (215). Obviously, Freundlich isotherm is widely used in the study of due to its ability to fit nearly all experimental adsorption–desorption data. In particular, this isotherm provides excellently fitting data of highly heterogeneous adsorbent systems. The limitation of Freundlich isotherm of being inappropriate over a wide concentration range is always ignored by researchers since a moderate concentration range is normally used in most biosorption studies.

Adsorption capacity is the most significant property of an adsorbent. It is defined as the value of amount of a specific adsorbate taken up by an adsorbent per unit mass of the adsorbent. This variable is governed by the nature of the adsorbent, such as pore and particle size distribution, specific surface area, cation exchange capacity, and surface functional groups. Besides, pH and temperature of the system may also affect the adsorption capacity of an adsorbent. In general, the adsorption capacities of most of the biosorbents (obtained from  $K_F$ ) are considerably low as compared with the commercially available activated carbons. Nevertheless, different types of biosorbents are still receiving intensive attraction from the researchers in view of their biosorption advantages and cost-effectiveness.

### 5.6.2.1.3 Temkin Isotherm

The Temkin model (216) takes into accounts of indirect interactions between the adsorbate molecules on adsorption isotherms. The derivation of Temkin isotherm assumes that as the surface of the adsorbent is occupied by the adsorbate, the heat of adsorption of all molecules in the layer would decrease linearly with coverage due to the indirect interactions. It makes the Temkin model differ from Freundlich model which implies a logarithmical decrease in the heat of adsorption. The Temkin equation proposes a linear decrease of adsorption energy as an increase in the degree of completion of the adsorption centers on an adsorbent. The equation is expressed as



$$q_e = \frac{RT}{b} \ln a C_e \quad (5.9)$$

where

$a$  = the Temkin isotherm constant

$b$  = the Temkin constant related to the heat of adsorption

The linear form of the Temkin equation (Equation 5.10) is applicable to analyze the adsorption data at moderate concentrations. Both constants  $a$  and  $b$  can be determined from a plot of  $q_e$  versus  $\ln C_e$ :

$$q_e = \frac{RT}{b} \ln a + \frac{RT}{b} \ln C_e \quad (5.10)$$

The simple assumptions made within the Temkin equation cause the derivation for this equation not well suited for a complex phenomenon involved in liquid-phase adsorption. Unlike gas-phase adsorption, the adsorbed molecules are not necessarily organized in a tightly packed structure with identical orientation in liquid-phase adsorption. In addition, the formation of micelles from the adsorbed molecules and the presence of solvent molecules add to the complexity of adsorption in liquid phase. In fact, liquid-phase adsorption is also greatly impacted by other factors such as pH, solubility of the adsorbate in the solvent, and temperature and surface chemistry of the adsorbent. For this reason, this equation is rarely used for the representation of experimental data of complex systems.

#### 5.6.2.1.4 BET Model

The first isotherm for multimolecular layer adsorption was derived by Brunauer, Emmer, and Teller (217). This major advance in adsorption theory, the so-called BET theory, has solved the constraint found in Langmuir isotherm. Assuming the adsorbent surface is composed of fixed individual sites and molecules can be adsorbed more than one layer thick on the surface of the adsorbent, this model suggests a random distribution of sites covered by one, two, three, or more adsorbate molecules. Besides, the model is made based on the assumptions that there is no interaction between each adsorption layer, and the Langmuir theory can be applied to each layer. In other words, the same kinetics concept proposed by Langmuir is applied to this multiple layering process, that is, the rate of adsorption on any layer is equal to the rate of desorption from that layer. The simplified form of the BET equation is written as

$$q_e = q_{\max} \frac{K_B C_e}{(C_e - C_s)[1 + (K_B - 1)(C_e/C_s)]} \quad (5.11)$$

where

$q_{\max}$  = mass of the adsorbate adsorbed/mass of the adsorbent for a complete monolayer

$C_s$  = concentration of the adsorbate at saturation of all layers

$K_B$  = constant related to energy of adsorption

Equation 5.11 can be converted into a linear form:

$$\frac{C_e}{(C_s - C_e)q} = \frac{1}{K_B q_{\max}} + \left( \frac{K_B - 1}{K_B q_{\max}} \right) \left( \frac{C_e}{C_s} \right) \quad (5.12)$$

The BET model is based on an ideal assumption that all sites are energetically identical along with no horizontal interaction between the adsorbed molecules. As a result, it may be applicable for systems involving heterogeneous materials and simple nonpolar gases, but it is not valid for complex systems dealing with heterogeneous adsorbent such as biosorbents and adsorbates. Consequently, it has lost its popularity in the interpretation of liquid-phase adsorption data for complex solids.

#### 5.6.2.1.5 D–R Isotherm

By not assuming a homogeneous surface or constant adsorption potential, Dubinin and Radushkevich (218) have proposed another equation used in the analysis of isotherms. This model suggests the close relationship between characteristic adsorption curve and porous structure of the biosorbent. Apart from estimating the porosity and the characteristics of adsorption, this model can also be used to determine the apparent free energy of the adsorption process. The D–R isotherm is expressed as

$$q_e = Q_m \exp(-K\varepsilon^2) \quad (5.13)$$

where

$K$  = the constant related to the adsorption energy

$Q_m$  = the adsorption capacity of the adsorbent per unit mass

$\varepsilon$  = Polanyi potential which is correlated to temperature

The D–R equation can be rearranged into a linear form:

$$\ln q_e = \ln Q_m - K\varepsilon^2 \quad (5.14)$$

The slope of the plot  $\ln q_e$  versus  $\varepsilon^2$  gives  $K$  and the intercept yields the adsorption capacity,  $Q_m$ . The constant  $K$  is related to the mean free energy of adsorption ( $E$ ) per mole of the adsorbate during the transportation process from infinite distance in solution to the surface of the solid. Thus,  $E$  can be calculated from the  $K$  value using the relation

$$E = \frac{1}{\sqrt{2K}} \quad (5.15)$$

In fact, this energy  $E$  can be computed using the following relationship (219):

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (5.16)$$

Since the D–R isotherm is temperature dependent, a characteristic curve with all the suitable data lying on the same curve can be obtained by plotting the adsorption data at different temperatures ( $\ln q_e$  versus  $\varepsilon^2$ ). In other words, the applicability of the D–R equation in expressing the adsorption equilibrium data is confirmed if the identity curve is obtained. Apparently, the validity of the ascertained parameters would be questionable when the fitting procedure gives high correction values, but the characteristic curve generated from the analyzed data shows deviation. Nevertheless, the characteristic curve of biosorption systems is rarely examined as the experiments were usually conducted at one temperature. The disadvantage of the D–R isotherm is its suitability for only an intermediate range of adsorbate concentrations as it may exhibit unrealistic asymptotic behavior.

### 5.6.2.1.6 Hasley Isotherm

Like the Freundlich isotherm, the Hasley model (220) is suitable for multilayer adsorption. The advantage of this isotherm is its usage to confirm the heteroporous nature of the adsorbent by excellent fitting of the experimental data to this model. The Hasley equation is expressed as

$$q_e = \text{Exp}\left(\frac{\ln k_H - \ln C_e}{n}\right) \quad (5.17)$$

where

$k_H$  = the Hasley isotherm constant  
 $n$  = the Hasley isotherm exponent

### 5.6.2.1.7 H-J Isotherm

The H-adsorption isotherm (221) is suitable for multilayer adsorption. This model suggests the existence of a heterogeneous pore distribution in the adsorbent. The H-J isotherm is given as follows:

$$q_e = \sqrt{\frac{A_H}{B_2 + \log C_e}} \quad (5.18)$$

where

$A_H$  = isotherm parameter  
 $B_2$  = isotherm constant

## 5.6.2.2 Three-Parameter Isotherms

There are cases when the two-parameter models are not competent enough to correlate and describe the equilibrium data. For this reason, models involving more than two parameters are needed to interpret the data. A particular model might be inapplicable in a certain situation, while in some cases more than one model can explain the biosorption mechanism. Some available three-parameter isotherms for the prediction of biosorption experimental data are presented.

### 5.6.2.2.1 Redlich-Peterson Isotherm

By combining elements from both the Langmuir and Freundlich equations, the Redlich-Peterson (R-P) isotherm model (222) suggests that the adsorption mechanism is a hybrid of the two and does not follow ideal monolayer adsorption. The isotherm model is capable to characterize adsorption equilibrium over a wide concentration range:

$$q_e = \frac{K_{RP}C_e}{1 + a_{RP}C_e^\beta} \quad (5.19)$$

where  $K_{RP}$ ,  $a_{RP}$ , and  $\beta$  are the R- parameters. The exponent  $\beta$  lies between 0 and 1.

Its limiting behavior is summarized here: when  $\beta = 1$ , the R-P equation resembles the Langmuir equation:

$$q_e = \frac{K_{RP}C_e}{1 + a_{RP}C_e} \quad (5.20)$$

If  $\beta = 0$ , the equation represents Henry's law:

$$q_e = \frac{K_{RP}C_e}{1 + a_{RP}} \quad (5.21)$$

Since the  $\beta$  values are close to unity in most biosorption cases, the adsorption data are rather be fitted with the Langmuir model.

The linearized form of Equation 5.19 is written as

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \ln a_{RP} + \beta \ln C_e \quad (5.22)$$

The linear forms of the equations allow determination of the parameters of the Langmuir and Freundlich models. However, it is not possible to obtain the parameters of the R–P isotherms from the linear equation because R–P isotherm incorporates three parameters. To solve this problem, a minimization procedure has to be adopted to verify the parameters of Equation 5.22 by maximizing the correlation coefficients between the experimental data points and those from theoretical model predictions with the solver add-in function for Microsoft Excel.

#### 5.6.2.2.2 Sips Isotherm

To avoid the problem of continuing increase in the adsorbed amount with rising concentration as observed in the Freundlich model, Sips isotherm was proposed (223). In fact, the Sips expression (Equation 5.21) is similar to the Freundlich isotherm, and differs only on the finite limit of the adsorbed amount at sufficiently high concentration:

$$q_e = q_{\max} \frac{(K_S C_e)^\gamma}{1 + (K_S C_e)^\gamma} \quad (5.23)$$

where  $K_S$  = Sips isotherm constant

Besides, Equation 5.23 is akin to the Langmuir equation, Equation 5.1. The distinctive feature in Equation 5.23 is the presence of an additional parameter,  $\gamma$ . The parameter  $\gamma$  characterizes heterogeneity of the system, which could stem from the biosorbent or the adsorbate, or a combination of both. In the case  $\gamma$  is unity, Equation 5.23 is equivalent to Equation 5.3.

#### 5.6.2.2.3 Toth Equation

Both Freundlich and Sips equations have their limitations in describing an adsorption data. As discussed previously, Freundlich equation is not able to predict adsorption equilibria data at intense concentration, while Sips equation is invalid at the low concentration end. Obviously, both mentioned equations are not reduced to the correct Henry law type at the low concentration limit. To overcome this, Toth isotherm (224) which obeys Henry's law at low concentration and reaches an adsorption maximum at high concentration is proposed. The Toth isotherm is derived from the potential theory and it is capable to describe adsorption for heterogeneous systems. It assumes an asymmetrical quasi-Gaussian energy distribution with its left-hand side widened, that is, most sites have adsorption energy less than the mean value:

$$q_e = q_{\max} \frac{C_e}{[a_t + C_e^t]^{1/t}} \quad (5.24)$$

where

$a_t$  = adsorptive potential constant

$t$  = heterogeneity coefficient of the adsorbent ( $0 < t \leq 1$ )

Toth equation possesses a parameter to characterize the heterogeneity of the system. The Toth equation reduces to the Langmuir equation when a surface is homogeneous,  $t = 1$ .

### 5.6.3 KINETIC MODELING OF BIOSORPTION IN A BATCH SYSTEM

High adsorption capacity and fast adsorption rate are two important criteria for an ideal adsorbent. As the efficiency of the adsorption process is strongly dependent on the rate of the adsorbate to attach onto the surface of the adsorbent, kinetic studies appear as an important step in the selection of a suitable adsorbent. Apart from reflecting the factors affecting the adsorption process, results from kinetic studies also provide prediction on the adsorption rate. In adsorption processes, the three commonly used kinetic models are the intraparticle diffusion model, pseudo-first-order kinetic model, and pseudo-second-order kinetic model. These kinetic models are applicable to examine the rate determining mechanism of the adsorption process as well as the role of the adsorption surface, the chemical reaction involved, and/or diffusion mechanisms. In practice, kinetic studies were carried out in batch reactions using various adsorbent doses and particle sizes, initial adsorbate concentrations, agitation speeds, pH values, and temperatures along with different adsorbent and adsorbate types. Subsequently, the best-fitting kinetic rate equation is determined using linear regression. To confirm that the experimental data is in good agreement with the kinetic rate equations using the coefficients of determination, the linear least-square method is always applied to the linearly transformed kinetic rate equations.

Generally, the mechanism of adsorbate removal by adsorption is postulated as in the following steps:

1. Bulk diffusion: transport of adsorbate from the bulk solution to the surface of the adsorbent
2. Film diffusion: diffusion of adsorbate through the boundary layer to the surface of the adsorbent
3. Pore diffusion or intraparticle diffusion: migration of adsorbate from the surface to within the particle's pores
4. Adsorption: adsorption of adsorbate on the active sites that are available on the internal surface of the pores

It has been demonstrated in many studies that the bulk diffusion can be ignored providing sufficient stirring to avoid particle and solute gradients in the batch system. Therefore, the adsorption dynamics can be approximated by three consecutive steps 2 through 4 only. A rapid uptake which is immeasurably fast occurs in the adsorption process, in the last step of the mechanism. It is suggested that this step contributes no resistance and it can be considered as an instantaneous process especially in the case of physical adsorption. As a result, the overall rate of the adsorption process is controlled by either film or intraparticle diffusion, or by a combination of both.

In the case of chemical reactions, the adsorption rate may be controlled by its own kinetic rates. Not only the diffusion equations but also the boundary conditions and the adsorption isotherm equation for a complete modeling of kinetics should be taken into account since the adsorption kinetics provide valuable insights into the practical application of the process design and operation control. It has hence led to a complicated system of equations. However, the system is often possible to be simplified by separating the diffusion steps. Based on the assumptions that the initial adsorption rate was characterized by external diffusion and was controlled by intraparticle diffusion, the diffusion mechanisms were considered independently.

The film diffusion is an important rate-controlling step in the first step of adsorption. The change in adsorbate concentration with respect to time is presented as follows:

$$\frac{dC}{dt} = -k_L A(C - C_s) \quad (5.25)$$

where

$C$  = bulk liquid phase concentration of the adsorbate at any time  $t$

$C_s$  = surface concentration of the adsorbate

$k_L$  = external mass transfer coefficient

$A$  = specific surface area for mass transfer

It is assumed that during the initial stage of adsorption, the intraparticle resistance is negligible and the transport is mainly due to film diffusion mechanism. The surface concentration of the adsorbate,  $C_s$  can be ignored and  $C = C_0$  at  $t = 0$ . With these assumptions Equation 5.25 can be written in a simplified form:

$$\left[ \frac{d(C/C_0)}{dt} \right] = -k_L A \quad (5.26)$$

### 5.6.3.1 Intraparticle Diffusion Model

Weber and Morris (225) developed the intraparticle diffusion model to describe the intraparticle diffusion by correlating adsorption capacity to effective diffusivity of the adsorbate within the particle. The model is expressed as

$$q_t = f \left( \frac{Dt}{r_p^2} \right)^{1/2} = K_{WM} t^{1/2} \quad (5.27)$$

where

$r_p$  = particle radius

$D$  = effective diffusivity of solutes within the particle

$q_t$  = adsorption capacity at time  $t$

$K_{WM}$  = intraparticle diffusion rate constant

Intraparticle diffusion is the only rate determining step, the plot of  $q$  versus  $t^{1/2}$  should give a straight-line passing through the origin. The intraparticle diffusion rate constant  $K$  can be obtained from the slope of the straight-line. However, the adsorption process may involve some other mechanisms if the adsorption data exhibit multilinear plots. The first shaper portion is a good evidence of a significant external resistance to mass transfer surrounding the particles in the early stage of adsorption. The intraparticle diffusion dominates in the second linear portion, which is a gradual adsorption stage. Eventually, the intraparticle diffusion starts to slow down due to the extremely low solute concentration in solution in the third portion. The third portion is also recognized as the final equilibrium stage. Apparently, the adsorption mechanism can be rationalized by a good correlation of rate data in this model and  $K$  values can be determined by linearization of the curve  $q = f(t^{0.5})$ .

Owing to reasons such as (i) the greater mechanical obstruction to movement presented by the surface molecules or surface layers and (ii) the restraining chemical attractions between the adsorbate and the adsorbent, diffusion within the particle is a much slower process compared with the movement of the adsorbate from the solution to the external solid surface. During adsorption of the adsorbate in a batch system, adsorbate molecules reach at the adsorbent surface more quickly than they can diffuse into the solid. Accumulation of the adsorbate at the surface tends to establish a (pseudo)-equilibrium. Since the surface concentration is depleted by inward adsorption, further adsorption of the adsorbate can take place only at the same rate.

Pseudo-first- and pseudo-second orders are two simplified kinetic models which have been applied to test the adsorption kinetics of adsorbents. Basically, these two models take account of all the steps of adsorption including external film diffusion, intraparticle diffusion, and adsorption.

### 5.6.3.2 Pseudo-First-Order Kinetic Model

Pseudo-first-order kinetic model is also known as Lagergren model (226). In this model, adsorption is considered to be first order in adsorption capacity and chemisorption is the rate-limiting step, and hence it only predicts the behavior over the "whole" range of studies supporting the validity. In

spite of its limitation, this model has been widely used to characterize the adsorption behavior of an adsorbate. The Lagergren first-order rate expression based on solid capacity is generally written as

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (5.28)$$

where

$q_e$  = adsorption capacity at equilibrium state

$q_t$  = adsorption capacity at time  $t$

$k_1$  = rate constant of pseudo-first-order adsorption

Integration of Equation 5.28 with the boundary conditions at  $t = 0$ ,  $q_t = 0$ , and at  $t = t$ ,  $q_t = q_t$  results in

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5.29)$$

The nonlinear form of Equation 5.27 is given as

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (5.30)$$

Hypothetically, the straight-line plots of  $\ln(q_e - q_t)$  against  $t$  of Equation 5.29 should be made at different initial adsorbate concentrations to verify the rate constant and equilibrium adsorbate uptake. A straight-line of  $\ln(q_e - q_t)$  versus  $t$  confirms the applicability of this kinetic model. The  $q_e$  value obtained by this method is always compared with the experimental value. Even though the least-square fitting process yields a high correlation coefficient, a reaction cannot be classified as first order if a large discrepancy in the  $q_e$  values is observed. A time lag resulted from external mass transfer or boundary layer diffusion at the beginning of the adsorption process could be the reason for the difference in  $q_e$  values. In this case, nonlinear procedure fitting of Equation 5.30 appears as an alternative way to predict  $q_e$  and  $k_1$ , although this is not a common exercise.

### 5.6.3.3 Pseudo-Second-Order Kinetic Model

Since the system's kinetics determines adsorbate residence time and the reactor dimensions, predicting the rate of adsorption for a given system is among the most important factors in adsorption system design. Although the adsorption capacity is strongly dependent on various factors such as the nature of the adsorbate, initial adsorbate concentration, temperature, pH of solution and adsorbent particle size, a kinetic model is only concerned with the effect of observable parameters on the overall rate.

Ho and McKay's pseudo-second-order model (227) is derived on the basis of the adsorption capacity of the solid phase. This model can be expressed as

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (5.31)$$

where  $k_2$  = rate constant of pseudo-second-order adsorption

Integration of Equation 5.31 with the boundary conditions at  $t = 0$ ,  $q = 0$ , and at  $t = t$ ,  $q_t = q_t$ , yields

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t \quad (5.32)$$



Equation 4.32 can be converted into linear form as

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (5.33)$$

Ho and McKay equation is applicable to most adsorption systems for the entire experimental duration of adsorption using different adsorbate concentrations and adsorbent dosages. Most importantly, it allows determination of adsorption capacity, pseudo-second-order rate constant, and initial adsorption rate without prior knowledge of experimental parameters.

#### 5.6.4 CONTINUOUS PACKED-BED SYSTEM IN THE BIOSORPTION OF HEAVY METALS

The batch adsorption method is feasible to adopt for an adsorption system involving small volumes of adsorbate. However, for large-scale application of biosorption process, continuous flow treatments would be the better choice. In this method, adsorbates in solution are fed continuously to either the top or the bottom of a stationary bed of solid adsorbent. The amount of the adsorbate being adsorbed increases as a function of time and an unsteady-state condition prevails. In the adsorption process under continuous flow conditions, the equilibrium between adsorption and desorption is rarely achieved. The adsorbent is usually regenerated for reuse when the adsorptive capacity of the adsorbent is approached. Since this type of test conditions provides a closer simulation of commercial systems, it is commonly applied in the assessment of the suitability of an adsorbent for a particular adsorbate. Among all the different experimental setups, the packed-bed column is perhaps the most effective device for continuous operations.

In a downflow packed-bed column, initially, when the feed adsorbate solution moves through the column, it is in contact with the fresh adsorbent at the top of the column. As the solution flows down the column, most of the adsorbate is adsorbed progressively from the liquid onto the adsorbent. The concentration of the adsorbate in the effluent remains either very low or even untraceable or as the adsorbate solution passes through the adsorption zone, the adsorbate is either being removed partially or completely. The length of the adsorption zone is somewhat arbitrary as it is dependent of the value of the adsorbate concentration selected for its lower boundary. Adsorbate concentration in the effluent rises slowly if more adsorbate solution enters the column due to equilibrium and kinetic factors. When the upper portion of packing adsorbent is saturated with the adsorbate, the adsorption zone will move down the column like a slowly moving wave. Finally, the lower edge of the adsorption zone arrives at the bottom of the column, leading to a remarkable increase in adsorbate concentration in the effluent. With this rapid rise, the flow is stopped as little additional adsorption takes place with the entire bed approaching an equilibrium state with the feed. This point is referred to as the breakthrough point. The plot of adsorbate effluent concentration versus time is known as the breakthrough curve and it can be used to describe the performance of a continuous packed bed.

There are several factors that affect the breakthrough point and the breakthrough curve, such as the nature of the adsorbate and the adsorbent, geometry of the column, and the operating conditions. The breakthrough point usually increases with increasing bed height, reducing adsorbent's particle size, and with decreasing flow rate. The general position of the breakthrough curve along the time or volume axis may indicate the loading behavior of the adsorbate to be removed from a solution in a fixed bed. It is often expressed in terms of normalized concentration defined as the ratio of effluent adsorbate concentration to inlet adsorbate concentration ( $C/C_0$ ) as a function of time or volume of the effluent ( $V_{eff}$ ) for a given bed height. The breakthrough curve would approach a straight vertical line if the adsorption isotherm were favorable and if the adsorption rate were infinite. As the mass transfer rate decreases, the breakthrough curve becomes less sharp. It is noteworthy that the breakthrough curves are diffuse and exhibit an S-shape since the mass transfer is always finite.

A number of simple mathematical models have been developed to predict the dynamic behavior of the column. Various models that are used to characterize the fixed-bed performance for the bio-sorption process are presented here.

#### 5.6.4.1 Adams–Bohart Model

The Adams–Bohart model (228) is originally developed for gas adsorption. The adsorption is an equation used to characterize the relationship between  $C/C_0$  and  $t$  for the adsorption of chlorine on charcoal in a fixed-bed column. It assumes that the adsorption rate is proportional to both the residual capacity of the adsorbent and the concentration of the adsorbing species. Regardless of the phase of the adsorbate, its overall approach can be applied to quantitative description of other systems. The solution of the differential equations for mass transfer rate in solid and liquid phases makes the Adams–Bohart model applicable to fixed-bed column of different biosorption applications. The linear form of the model is shown in Equation 5.32:

$$\ln \frac{C}{C_0} = k_{AB} C_0 t - k_{AB} N \frac{Z}{U_0} \quad (5.34)$$

where

$C$  = adsorbate concentration remaining at each contact time

$C_0$  = initial adsorbate concentration

$k_{AB}$  = Adams–Bohart kinetic constant

$N$  = metal concentration in the bulk liquid

$Z$  = bed depth of column

$U_0$  = linear velocity calculated by dividing the flow rate by the column's sectional area

It is noteworthy that when  $t \rightarrow \infty$ ,  $N \rightarrow N_0$ , where  $N_0$  is the saturation concentration. Equation 5.32 is derived based on the assumption of low concentration field where  $C < 0.15C_0$  and it is generally valid in the initial part of the breakthrough. Therefore, this model is often utilized in describing the initial part of the breakthrough curve only. Values describing the characteristic operational parameters of the column can be determined from a plot of  $\ln C/C_0$  against  $t$  at a given bed height and flow rate.

#### 5.6.4.2 Bed Depth–Service Time Model

Starting from the Adams and Bohard model, the bed depth–service time (BDST) model (228) correlates the service time ( $t$ ) with the process variables by ignoring intraparticle mass resistance and external film resistance. This model is commonly used for determining the capacity of fixed bed at different breakthrough values. By assuming that the adsorbate is adsorbed onto the adsorbent surface directly, this model states that the service time for a column is given by

$$t = \frac{N_0}{C_0 U_0} Z - \frac{1}{K_a C_0} \ln \left( \frac{C_0}{C} - 1 \right) \quad (5.35)$$

where

$K_a$  = rate constant in BDST

$N_0$  = adsorption capacity

The equation is reduced to Equation 5.35 at 50% breakthrough ( $C_0/C = 2$ ) and  $t = t_{0.5}$

$$t_{0.5} = \left( \frac{N_0}{C_0 U_0} \right) Z \quad (5.36)$$

or

$$t_{0.5} = \text{constant} \times Z \quad (5.37)$$

If the adsorption data fits the model, a straight-line passing through the origin should be obtained in a plot of BDST at 50% breakthrough against bed depth using Equation 5.36.

#### 5.6.4.3 Yoon–Nelson Model

Yoon–Nelson model (229) is a relatively simple theoretical model as it does not require detailed information on the adsorbent and solute characteristics, adsorbent type, and on the physical properties of adsorption bed adsorbent. It assumes the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorption of the adsorbate and the probability of adsorbate breakthrough on the adsorbent. The Yoon and Nelson equation regarding a single-component system is given by

$$\ln \frac{C}{C_0 - C} = k_{YN}t - \tau k_{YN} \quad (5.38)$$

where

$k_{YN}$  = Yoon and Nelson rate constant

$t$  = time required for 50% adsorbate breakthrough

$\tau$  = breakthrough (sampling) time

Calculation of theoretical breakthrough curves for a single-component system requires the determination of the parameters  $k_{YN}$  and  $\tau$  for the adsorbate of interest. These values may be determined from the available experimental data. If the model adequately describes the experimental data, a straight-line should be obtained by a plot of  $\ln C/(C_0 - C)$  versus sampling time ( $t$ ), the slope and intercept of which are  $k_{YN}$  and  $\tau k_{YN}$ , respectively.

#### 5.6.4.4 Thomas Model

The Thomas model (230) appears as one of the most commonly used approximate models based on the assumption of Langmuir kinetics of adsorption–desorption and no axial dispersion. This model is usually used to obtain information on the maximum adsorption capacity of an adsorbate in column design. By considering the rate driving force obeys second-order reversible reaction kinetics, the expression of Thomas model for an adsorption column is given as follows:

$$\frac{C}{C_0} = \frac{1}{1 + \exp(k_{Th}/Q(q_0X - C_0V_{eff}))} \quad (5.39)$$

where

$k_{Th}$  = Thomas rate constant

$Q$  = Flow rate

$q_0$  = Maximum solid-phase concentration of the solute

$X$  = Amount of adsorbent in the column

$V_{eff}$  = Effluent volume

The Thomas model can be converted into linear form as follows:

$$\ln \left( \frac{C_0}{C} - 1 \right) = \frac{k_{Th}q_0X}{Q} - \frac{k_{Th}C_0}{Q} V_{eff} \quad (5.40)$$

A plot of  $\ln [(C_0/C) - 1]$  against  $t$  at a given flow rate allows determination of the kinetic coefficient  $k_{Th}$  and the adsorption capacity of the bed  $q_0$ .

#### 5.6.4.5 Clark Model

Clark (231) defined a new simulation of breakthrough curves which combined the Freundlich equation and the mass transfer concept. The equation generated based on this model has the following form:

$$\frac{C}{C_0} = \left( \frac{1}{1 + Ae^{-rt}} \right)^{1/n-1} \quad (5.41)$$

with

$$A = \left( \frac{C_0^{n-1}}{C_{break}^{n-1}} - 1 \right) e^{rt_{break}} \quad (5.42)$$

and

$$R(n-1) = r \quad \text{and} \quad R = \frac{k_{Cl}}{U_0} v \quad (5.43)$$

where

$C_{break}$  = Outlet concentration at breakthrough (or limit effluent concentration)

$t_{break}$  = Time at breakthrough

$k_{Cl}$  = Clark rate constant

$v$  = Migration rate

For a particular adsorption process on a fixed bed and a chosen treatment objective, values of  $A$  and  $r$  can be determined using Equation 5.43 by nonlinear regression analysis, enabling the prediction of the breakthrough curve according to the relationship between  $C/C_0$  and  $t$  in Equation 5.43.

#### 5.6.5 RESPONSE SURFACE METHODOLOGY

Response surface methodology (RSM) is a collection of mathematical and statistical techniques for designing experiments, building models, evaluating the effects of variables, and searching optimum conditions of variables to predict targeted responses. It can be considered as an important branch of experimental design and a critical technology particularly in developing new processes, optimizing their performance, and improving design and formulation of new products. Its great applications would be in situations that involve a large number of variables influencing the performance measure or quality characteristic of the product or process. This kind of performance measure or quality characteristic is termed as the response. Most real-world applications for RSM will involve more than one response.

As such, identifying and fitting an appropriate response surface model in heavy metal treatment process can be seen as an attractive approach to improve the removal rate, reduced process variability, time, and overall costs. Moreover, the factors that influence the experiments are identified, optimized, and possible synergic or antagonistic interactions that may exist between factors can be evaluated. There are three main steps involved in the development and optimization process: (i) experimental design, (ii) modeling, and (iii) optimization.

Optimization of a process could be performed either by empirical or statistical methods. However, the empirical method is time consuming and does not necessarily enable an effective optimization.

This could be solved through the statistics-based procedure, RSM. The optimization process by RSM involves three major steps:

1. Performing statistically designed experiments
2. Estimating the coefficients in a mathematical model
3. Predicting the response and checking the adequacy of the model

RSM represents the independent process variables in this quantitative form (232):

$$Y = f(A_1, A_2, A_3, \dots, A_n) \quad (5.44)$$

where

$Y$  = the amount of metal adsorbed (mg/L)

$f$  = response function

$A_1, A_2, A_3, \dots, A_n$  = the independent variables

Response surface is obtained by plotting the expected response but the value of  $f$  is unknown and can be very complicated. So RSM approximates its value by a suitable lower-order polynomial. If response varies in a linear manner, the response can be represented by this linear function equation as

$$Y = b_0 + b_1A_1 + b_2A_2 + \dots + b_nA_n \quad (5.45)$$

But if curvature is there in the system, a higher-order polynomial such as the quadratic model is used which can be stated in the form of the following equation:

$$Y = b_0 + \sum b_iA_i + \sum b_{ii}A_i^2 + \sum b_{ij}A_iA_j \quad (5.46)$$

where

$b_0$  = offset term

$A_i$  = first-order main effect

$A_{ii}$  = second-order main effect

$A_{ij}$  = interaction effect

The application of RSM in the adsorption studies for heavy metals removal can minimize the number of experiments involved and optimize the effective parameters collectively (233–235).

## 5.7 CONCLUSIONS

The application of low-cost adsorbents in heavy metals removal will make the process highly economical and competitive particularly for environmental applications in detoxifying effluents from metal-plating and metal-finishing operations, mining and ore processing operations, battery and accumulator manufacturing operations, thermal power generation (coal-fired plants in particular), nuclear power generation, and so on. A number of investigations have demonstrated that biosorption is a useful alternative to the conventional systems for the removal of heavy metals from aqueous solution. This technology need not necessarily replace the conventional treatment routes but may complement them.

The adsorption capacity of low-cost materials normally can be improved by pretreatment or modification using physical or chemical methods. Chemical modification in general improved the

adsorption capacity of adsorbents probably due to the higher number of active binding sites after modification, better ion-exchange properties, and due to the formation of new functional groups that favors metal uptake. Although chemically modified low-cost adsorbents can enhance its adsorptivity toward heavy metals, the cost of chemicals used and methods of modification also have to be taken into consideration in order to produce “low-cost” adsorbents.

Although excellent removal capabilities were apparent for several low-cost adsorbents, the utilization of these materials in industrial-scale applications is still far from reality. All these arguments converge into one conclusion: more effort is required to implement low-cost materials as adsorbents for removal of heavy metals. The researchers from various scientific backgrounds, from engineering to biochemistry, working together, will make a significant contribution to elucidating the bio-sorption mechanisms. Further testing in real wastewater should be conducted, and at the same time, appropriate mathematical models need to be developed. It is desirable to have a low-cost adsorbent with a wide range of metal affinities as this will be particularly useful for industrial effluents that carry more than one type of metals.

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