CHAPTER II

LITERATURE REVIEW
2.1. Applications, Toxicity and Effects of Heavy metals under consideration

2.1.1. Copper

Copper is a reddish metal with a face-centered cubic crystalline structure. It reflects red and orange light and absorbs other frequencies in the visible spectrum, due to its band structure, so it as a nice reddish colour. It is malleable, ductile, and an extremely good conductor of both heat and electricity. It is softer than iron but harder than zinc and can be polished to a bright finish. It is found in group Ib of the periodic table, together with silver and gold. Copper has low chemical reactivity. In moist air it slowly forms a greenish surface film called patina; this coating protects the metal from further attack.

Table 2.1: Various properties and specific values of Copper

<table>
<thead>
<tr>
<th>S No.</th>
<th>PROPERTIES</th>
<th>VALUES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Atomic number</td>
<td>29</td>
</tr>
<tr>
<td>2.</td>
<td>Atomic mass</td>
<td>63.546 g.mol⁻¹</td>
</tr>
<tr>
<td>3.</td>
<td>Electronegativity according to Pauling</td>
<td>1.9</td>
</tr>
<tr>
<td>4.</td>
<td>Density</td>
<td>8.9 g.cm⁻³ at 20°C</td>
</tr>
<tr>
<td>5.</td>
<td>Melting point</td>
<td>1083 °C</td>
</tr>
<tr>
<td>6.</td>
<td>Boiling point</td>
<td>2595 °C</td>
</tr>
<tr>
<td>7.</td>
<td>Vanderwaals radius</td>
<td>0.128 nm</td>
</tr>
<tr>
<td>8.</td>
<td>Ionic radius</td>
<td>0.096 nm (+1); 0.069 nm (+3)</td>
</tr>
<tr>
<td>9.</td>
<td>Isotopes</td>
<td>6</td>
</tr>
<tr>
<td>10.</td>
<td>Electronic shell</td>
<td>[Ar] 3d¹⁰ 4s¹</td>
</tr>
<tr>
<td>11.</td>
<td>Energy of first ionisation</td>
<td>743.5 kJ.mol⁻¹</td>
</tr>
<tr>
<td>12.</td>
<td>Energy of second ionisation</td>
<td>1946 kJ.mol⁻¹</td>
</tr>
<tr>
<td>13.</td>
<td>Standard potential</td>
<td>+ 0.522 V (Cu⁺ / Cu⁻) ; + 0.345 V (Cu²⁺ / Cu⁻)</td>
</tr>
<tr>
<td>14.</td>
<td>Discovered by</td>
<td>The ancients</td>
</tr>
</tbody>
</table>

Most copper is used for electrical equipment (60%); construction, such as roofing and plumbing (20%) industrial machineri, such as heat exchangers
(15%) and alloys (5%). The main long established copper alloys are bronze, brass (a copper-zinc alloy), copper-tin-zinc, which was strong enough to make guns and cannons, and was known as gun metal, copper and nickel, known as cupronickel, which was the preferred metal for low-denomination coins. Copper is ideal for electrical wiring because it is easily worked, can be drawn into fine wire and has a high electrical conductivity.

Copper is a very common substance that occurs naturally in the environment and spreads through the environment through natural phenomena. It is applied in industries and in agriculture. The production of copper has lifted over the last decades and due to this copper quantities in the environment have expanded. Rivers are depositing sludge on their banks that is contaminated with copper, due to the disposal of copper-containing wastewater. Copper enters the air, mainly through release during the combustion of fossil fuels, and remains there for an eminent period of time, before it settles when it starts to rain. It will than end up mainly in soils. Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. A few examples of human activities that contribute to copper release have already been named. Other examples are mining, metal production, wood production and phosphate fertilizer production. Because copper is released both naturally and through human activity it is very widespread in the environment.

Copper is often found near mines, industrial settings, landfills and waste disposals. Most copper compounds will settle and be bound to either water sediment or soil particles. Soluble copper compounds form the largest threat to human health. Usually water-soluble copper compounds occur in the environment after release through application in agriculture. World production of copper amounts to 12 million tonnes a year and exploitable reserves are around 300 million tonnes, which are expected to last for only another 25 years. About 2 million tonnes a year are reclaimed by recycling. Today copper is mined as major deposits in Chile, Indonesia, USA, Australia and Canada, which together account for around 80% of the world’s copper. The main ore is a yellow copper-iron sulfide called chalcopryte (CuFeS₂).
Copper can be found in many kinds of food, in drinking water and in air. Because of that is absorbed in the eminent quantities of copper each day by eating, drinking and breathing. Although humans can handle proportionally large concentrations of copper, too much copper can still cause eminent health problems. Copper concentrations in air are usually quite low, so that exposure to copper through breathing is negligible. But people that live near smelters (that process copper ore into metal), do experience this kind of exposure. People that live in houses that still have copper plumbing are exposed to higher levels of copper than most people, because copper is released into their drinking water through corrosion of pipes. Occupational exposure to copper often occurs. In the work place environment, copper contagion can lead to a flu-like condition known as metal fever. This condition will pass after two days and is caused by over sensitivity.

Acne, allergies, alopecia, insomnia, nausea, spaciness, tooth decay, strokes, PMS, yeast infections, urinary tract infections, mood swings, kidney disorders, depression, cystic fibrosis, arthritis, anxiety, anorexia, multiple sclerosis, inflammation, pancreatic dysfunction, vitamin deficiencies, paranoia, migraines, libido decreased, nervousness, osteoporosis, senility, stuttering, phobias, diabetes, autism, estrogen dominance.

When copper ends up in soil, it strongly attaches to organic matter and minerals. As a result, it does not travel very far after release and hardly ever enters groundwater. In surface water, copper can travel great distances, either suspended as sludge particles or as free ions. Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On copper-rich soils only a limited number of plants have a chance of survival. That is why there is not much plant diversity near copper-disposing factories. Due to the effects upon plants copper is a serious threat to the productions of farmlands. Copper can seriously influence the proceedings of certain farmlands, depending upon the acidity of the soil and the presence of organic matter. Despite of this, copper-containing manures are still applied. Copper can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms. The decomposition of organic matter may seriously slow down because of this.
When the soils of farmland are polluted with copper, animals will absorb concentrations that are damaging to their health. Mainly sheep suffer a great deal from copper poisoning, because the effects of copper are manifesting at fairly low concentrations.

2.1.2. Cadmium

Cadmium is a lustrous, silver-white, ductile, very malleable metal. Its surface has a bluish tinge and the metal is soft enough to be cut with a knife, but it tarnishes in air. It is soluble in acids but not in alkalis. It is similar in many respects to zinc but it forms more complex compounds. About three-fourths of cadmium is used in Ni-Cd batteries, most of the remaining one-fourth is used mainly for pigments, coatings and plating, and as stabilizers for plastics. Cadmium has been used particularly to electroplate steel where a film of cadmium only 0.05 mm thick will provide complete protection against the sea. Cadmium has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission.

Table 2.2: Various properties and specific values of Cadmium

<table>
<thead>
<tr>
<th>S No.</th>
<th>PROPERTIES</th>
<th>VALUES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Atomic number</td>
<td>48</td>
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<tr>
<td>2.</td>
<td>Atomic mass</td>
<td>112.4 g.mol⁻¹</td>
</tr>
<tr>
<td>3.</td>
<td>Electronegativity according to Pauling</td>
<td>1.7</td>
</tr>
<tr>
<td>4.</td>
<td>Density</td>
<td>8.7 g.cm⁻³ at 20°C</td>
</tr>
<tr>
<td>5.</td>
<td>Melting point</td>
<td>321 °C</td>
</tr>
<tr>
<td>6.</td>
<td>Boiling point</td>
<td>767 °C</td>
</tr>
<tr>
<td>7.</td>
<td>Vanderwaals radius</td>
<td>0.154 nm</td>
</tr>
<tr>
<td>8.</td>
<td>Ionic radius</td>
<td>0.097 nm (+2)</td>
</tr>
<tr>
<td>9.</td>
<td>Isotopes</td>
<td>15</td>
</tr>
<tr>
<td>10.</td>
<td>Electronic shell</td>
<td>[Kr] 4d¹⁰ 5s²</td>
</tr>
<tr>
<td>11.</td>
<td>Energy of first ionisation</td>
<td>866 kJ.mol⁻¹</td>
</tr>
<tr>
<td>12.</td>
<td>Energy of second ionisation</td>
<td>1622 kJ.mol⁻¹</td>
</tr>
<tr>
<td>13.</td>
<td>Standard potential</td>
<td>-0.402 V</td>
</tr>
<tr>
<td>14.</td>
<td>Discovered</td>
<td>Fredrich Stromeyer in 1817</td>
</tr>
</tbody>
</table>
Cadmium can mainly be found in the earth’s crust. It always occurs in combination with zinc. Cadmium also consists in the industries as an inevitable by-product of zinc, lead and copper extraction. After being applied it enters the environment mainly through the ground, because it is found in manures and pesticides. Naturally a very large amount of cadmium is released into the environment, about 25,000 tons a year. About half of this cadmium is released into rivers through weathering of rocks and some cadmium is released into air through forest fires and volcanoes. The rest of the cadmium is released through human activities, such as manufacturing. No cadmium ore is mined for the metal, because more than enough is produced as a byproduct of the smelting of zinc from its ore, sphalerite (ZnS), in which CdS is a significant impurity, making up as much as 3%. Consequently, the main mining areas are those associated with zinc. World production is around 14,000 tonnes per year; the main producing country is Canada, with the USA, Australia, Mexico, Japan and Peru also being the major suppliers.

The various sources include tap water, fungicides, marijuana, processed meat, rubber, seafood (cod, haddock, oyster, tuna), sewage, tobacco, colas (especially from vending machines), tools, welding material, evaporated milk, airborne industrial contaminants, batteries, instant coffee, incineration of tires/rubber/plastic, refined grains, soft water, galvanized pipes, dental alloys, candy, ceramics, electroplating fertilizers, paints, motor oil and motor exhaust.

The symptoms and diseases include alopecia, anemia, arthritis, cancer, lung disease, cerebral hemorrhage, cirrhosis of the liver, enlarged heart, diabetes, emphysema, hypoglycemia, hypertension, impotence, infertility, kidney disease, learning disorders, migraines, inflammation, renal disease, osteoporosis, schizophrenia, strokes, vascular disease, high cholesterol, and growth is impaired, cardiovascular disease. Cadmium inhibits essential enzymes in the Krebs energy cycle. Cadmium directly damages nerve cells. It inhibits the release of acetylcholine and activates cholinesterase, resulting in a tendency for hyperactivity of the nervous system. By altering calcium and phosphorus metabolism, a toxic level of cadmium can contribute to arthritis, osteoporosis, and neuromuscular
diseases. Cadmium replaces zinc in the arteries, which contributes to arteries being brittle and inflexible. Cadmium accumulates in the kidneys, resulting in high blood pressure and kidney disease. Cadmium toxicity can alter calcium and vitamin D activity, resulting in cavities and tooth deformities.

Cadmium waste streams from the industries mainly end up in soils. The causes of these waste streams are for instance zinc production, phosphate ore implication and bio industrial manure. Cadmium waste streams may also enter the air through (household) waste combustion and burning of fossil fuels. Because of regulations only little cadmium now enters the water through disposal of wastewater from households or industries. Another important source of cadmium emission is the production of artificial phosphate fertilizers. Part of the cadmium ends up in the soil after the fertilizer is applied on farmland and the rest of the cadmium ends up in surface waters when waste from fertilizer productions is dumped by production companies. Cadmium can be transported over great distances when it is absorbed by sludge.

Cadmium strongly adsorbs to organic matter in soils. When cadmium is present in soils it can be extremely dangerous, as the uptake through food will increase. Soils that are acidified enhance the cadmium uptake by plants. This is a potential danger to the animals that are dependent upon the plants for survival. Cadmium can accumulate in their bodies, especially when they eat multiple plants.

Earthworms and other essential soil organisms are extremely susceptible to cadmium poisoning. They can die at very low concentrations and this has consequences for the soil structure. When cadmium concentrations in soils are high they can influence soil processes of microorganisms and threat the whole soil ecosystem. In aquatic ecosystems cadmium can bio accumulate in mussels, oysters, shrimps, lobsters and fish. The susceptibility to cadmium can vary greatly between aquatic organisms. Salt-water organisms are known to be more resistant to cadmium poisoning than freshwater organisms. Animals eating or drinking cadmium sometimes get high blood-pressures, liver disease and nerve or brain damage.
2.1.3. Chromium

Chromium is a lustrous, brittle, hard metal. Its colour is silver-gray and it can be highly polished. It does not tarnish in air, when heated it burns and forms the green chromic oxide. Chromium is unstable in oxygen, it immediately produces a thin oxide layer that is impermeable to oxygen and protects the metal below. Chromium main uses are in alloys such as stainless steel, in chrome plating and in metal ceramics. Chromium plating was once widely used to give steel a polished silvery mirror coating. Chromium is used in metallurgy to impart corrosion resistance and a shiny finish; as dyes and paints, its salts colour glass an emerald green and it is used to produce synthetic rubies; as a catalyst in dyeing and in the tanning of leather; to make molds for the firing of bricks. Chromium (IV) oxide (CrO₂) is used to manufacture magnetic tape.

Table 2.3: Various properties and specific values of Chromium

<table>
<thead>
<tr>
<th>S No.</th>
<th>PROPERTIES</th>
<th>VALUES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Atomic number</td>
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</tr>
<tr>
<td>2.</td>
<td>Atomic mass</td>
<td>51.996 g.mol⁻¹</td>
</tr>
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<td>3.</td>
<td>Electronegativity</td>
<td>1.6</td>
</tr>
<tr>
<td>4.</td>
<td>Density</td>
<td>7.19 g.cm⁻³ at 20°C</td>
</tr>
<tr>
<td>5.</td>
<td>Melting point</td>
<td>1907 °C</td>
</tr>
<tr>
<td>6.</td>
<td>Boiling point</td>
<td>2672 °C</td>
</tr>
<tr>
<td>7.</td>
<td>Vanderwaals radius</td>
<td>0.127 nm</td>
</tr>
<tr>
<td>8.</td>
<td>Ionic radius</td>
<td>0.061 nm (+3); 0.044 nm (+6)</td>
</tr>
<tr>
<td>9.</td>
<td>Isotopes</td>
<td>6</td>
</tr>
<tr>
<td>10.</td>
<td>Electronic shell</td>
<td>[Ar] 3d⁴ 4s²</td>
</tr>
<tr>
<td>11.</td>
<td>Energy of first ionisation</td>
<td>651.1 kJ.mol⁻¹</td>
</tr>
<tr>
<td>12.</td>
<td>Energy of second ionisation</td>
<td>1590.1 kJ.mol⁻¹</td>
</tr>
<tr>
<td>13.</td>
<td>Energy of first ionisation</td>
<td>2987 kJ.mol⁻¹</td>
</tr>
<tr>
<td>14.</td>
<td>Standard potential</td>
<td>-0.71 V (Cr²⁺ / Cr⁻)</td>
</tr>
<tr>
<td>15.</td>
<td>Discovered by</td>
<td>Vaughan in 1797</td>
</tr>
</tbody>
</table>
Chromium is mined as chromite (FeCr₂O₄) ore. Chromium ores are mined today in South Africa, Zimbabwe, Finland, India, Kazakhstan and the Philippines. A total of 14 million tonnes of chromite ore is extracted and USA. The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

Chromium and most trivalent chromium compounds have been listed by the National Toxicology Program (NTP) as having inadequate evidence for carcinogenicity in experimental animals. According to NTP, there is sufficient evidence for carcinogenicity in experimental animals for the following hexavalent chromium compounds; calcium chromate, chromium trioxide, lead chromate, strontium chromate, and zinc chromate. International Agency for Research on Cancer (IARC) has listed chromium metal and its trivalent compounds within Group 3 (The agent is not classifiable as to its carcinogenicity to humans.) Chromium is not regulated as a carcinogen by OSHA (29 CFR 1910 Subpart Z). ACGIH has classified chromium metal and trivalent chromium compounds as A4, not classifiable as a human carcinogen.

There are several different kinds of chromium that differ in their effects upon organisms. Chromium enters the air, water and soil in the chromium(III) and chromium(VI) form through natural processes and human activities. The main human activities that increase chromium(VI) concentrations are chemical, leather and textile manufacturing, electro painting and other chromium(VI) applications in the industry. Through coal combustion, chromium also ends up in air and through waste disposal chromium will end up in soils. Most of the chromium in air will eventually settle and end up in waters or soils. Chromium in soils strongly attaches to soil particles and as a result it will not
move towards groundwater. In water chromium will absorb on sediment and become immobile. Only a small part of the chromium that ends up in water will eventually dissolve. Chromium(III) is an essential element for organisms that can disrupt the sugar metabolism and cause heart conditions, when the daily dose is too low. Chromium(VI) is mainly toxic to organisms. It can alter genetic materials and cause cancer.

Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of chromium in the soil rises, this can still lead to higher concentrations in crops. Acidification of soil can also influence chromium uptake by crops. Plants usually absorb only chromium (III). This may be the essential kind of chromium, but when concentrations exceed a certain value, negative effects can still occur. Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal. In animals chromium can cause respiratory problems, a lower ability to fight disease, birth defects, infertility and tumor formation.

2.1.4. Nickel
Nickel is silvery-white, hard, malleable, and ductile metal. It is of the iron group and it takes on a high polish. It is a fairly good conductor of heat and electricity. In its familiar compounds nickel is bivalent, although it assumes other valences. It also forms a number of complex compounds. Most nickel compounds are blue or green. Nickel dissolves slowly in dilute acids but, like iron, becomes passive when treated with nitric acid. Finely divided nickel adsorbs hydrogen.
The major use of nickel is in the preparation of alloys. Nickel alloys are characterized by strength, ductility, and resistance to corrosion and heat. About 65% of the nickel consumed is used to make stainless steel, whose composition can vary but is typically iron with around 18% chromium and 8% nickel. 12% of all the nickel consumed goes into super alloys. The remaining 23% of consumption is divided between alloy steels, rechargeable batteries, catalysts and other chemicals, coinage, foundry products, and plating. Nickel is easy to work and can be drawn into wire. It resists corrosion even at high temperatures and for this reason it is used in gas turbines and rocked engines. Monel is an alloy of nickel and copper (e.g. 70% nickel, 30% copper with traces of iron, manganese and silicon), which is not only hard but can resist corrosion by sea water, so that it is ideal for propeller shaft in boats and desalination plants usually itching, which occurs up to 7 days before skin

<table>
<thead>
<tr>
<th>S No.</th>
<th>PROPERTIES</th>
<th>VALUES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Atomic number</td>
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</tr>
<tr>
<td>2.</td>
<td>Atomic mass</td>
<td>58.71 g.mol(^{-1})</td>
</tr>
<tr>
<td>3.</td>
<td>Electronegativity according to Pauling</td>
<td>1.8</td>
</tr>
<tr>
<td>4.</td>
<td>Density</td>
<td>8.9 g.cm(^{-3}) at 20°C</td>
</tr>
<tr>
<td>5.</td>
<td>Melting point</td>
<td>1453 °C</td>
</tr>
<tr>
<td>6.</td>
<td>Boiling point</td>
<td>2913 °C</td>
</tr>
<tr>
<td>7.</td>
<td>Vanderwaals radius</td>
<td>0.124 nm</td>
</tr>
<tr>
<td>8.</td>
<td>Ionic radius</td>
<td>0.069 nm (+2); 0.06 nm (+3)</td>
</tr>
<tr>
<td>9.</td>
<td>Isotopes</td>
<td>10</td>
</tr>
<tr>
<td>10.</td>
<td>Electronic shell</td>
<td>[Ar] 3d(^8) 4s(^2)</td>
</tr>
<tr>
<td>11.</td>
<td>Energy of first ionisation</td>
<td>735 kJ.mol(^{-1})</td>
</tr>
<tr>
<td>12.</td>
<td>Energy of second ionisation</td>
<td>1753 kJ.mol(^{-1})</td>
</tr>
<tr>
<td>13.</td>
<td>Energy of third ionisation</td>
<td>3387 kJ.mol(^{-1})</td>
</tr>
<tr>
<td>14.</td>
<td>Standard potential</td>
<td>- 0.25 V</td>
</tr>
<tr>
<td>15.</td>
<td>Discovered by</td>
<td>Alex Constedt 1751</td>
</tr>
</tbody>
</table>
eruption occurs. The primary skin eruption is erythematous, or follicular, which may be followed by skin ulceration. Nickel sensitivity, once acquired, appears to persist indefinitely.

Nickel and certain nickel compounds have been listed by the National Toxicology Program (NTP) as being reasonably anticipated to be carcinogens. The International Agency for Research on Cancer (IARC) has listed nickel compounds within group 1 (there is sufficient evidence for carcinogenicity in humans) and nickel within group 2B (agents which are possibly carcinogenic to humans). OSHA does not regulate nickel as a carcinogen. Nickel is on the ACGIH Notice of Intended Changes as a Category A1, confirmed human carcinogen.

Nickel is released into the air by power plants and trash incinerators. It will than settle to the ground or fall down after reactions with raindrops. It usually takes a long time for nickel to be removed from air. Nickel can also end up in surface water when it is a part of wastewater streams. The larger part of all nickel compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result. In acidic ground however, nickel is bound to become more mobile and it will often rinse out to the groundwater. There is not much information available on the effects of nickel upon organisms other than humans. High nickel concentrations on sandy soils can clearly damage plants; can diminish the growth rates of algae in surface waters.

Microorganisms can also suffer from growth decline due to the presence of nickel, but they usually develop resistance to nickel after a while. For animals nickel is an essential foodstuff in small amounts. But nickel is not only favourable as an essential element; it can also be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer on different sites within the bodies of animals, mainly of those that live near refineries. Nickel is not known to accumulate in plants or animals. As a result nickel will not bio magnify up the food chain.
2.2. Conventional Treatment techniques for heavy metal bearing waste streams

2.2.1. Chemical precipitation

Chemical precipitation is effective and by far the most widely used process in industry because it is relatively simple and inexpensive to operate [136]. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The forming precipitates can be separated from the water by sedimentation or filtration and the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation.

**Hydroxide precipitation:**

The most widely used chemical precipitation technique is hydroxide precipitation due to its relative simplicity, low cost and ease of pH control [118]. The solubility of the various metal hydroxides is minimized in the pH range of 8.0-11.0. The metal hydroxides can be removed by flocculation and sedimentation. A variety of hydroxides has been used to precipitate metals from wastewater, based on the low cost and ease of handling, lime is the preferred choice of base used in hydroxide precipitation at industrial settings.

Hydroxide precipitation process using Ca(OH)$_2$ and NaOH in removing Cu(II) and Cr(VI) ions from wastewater was evaluated [166]. The Cr(VI) was converted to Cr(III) using ferrous sulfate. Maximum precipitation of Cr(III) occurred at pH 8.7 with the addition of Ca(OH)$_2$ and the concentration of chromate was reduced from 30 to 0.01 mg/l. The cuproammonia was reduced by aeration and the optimum pH for maximum copper precipitation was about 12.0 for both Ca(OH)$_2$ and NaOH and the concentration of copper was reduced from 48.51 to 0.694 mg/l. To enhance lime precipitation, fly ash was used as a seed material [55]. The fly ash lime carbonation treatment increased the particle size of the precipitate and significantly improved the efficiency of heavy metal removal. The concentrations of chromium, copper, lead and zinc in effluents can be reduced from initial concentration of 100.0 mg/l to 0.08, 0.14, 0.03 and 0.45 mg/l, respectively. In hydroxide precipitation
process, the addition of coagulants such as alum, iron salts, and organic polymers can enhance the removal of heavy metals from wastewater.

Chemical coagulation and precipitation by lime to treat synthetic wastewater consisting of Zn, Cd, Mn and Mg at the concentration of 450, 150, 1085 and 3154 mg/l, respectively. He found that the optimum pH was more than 9.5. Moreover, if coagulant was added, the residual concentration of heavy metal can be decreased further. Although widely used, hydroxide precipitation also has some limitations. Firstly, hydroxide precipitation generates large volumes of relatively low density sludge, which can present dewatering and disposal problems. Secondly, some metal hydroxides are amphoteric, and the mixed metals create a problem using hydroxide precipitation since the ideal pH for one metal may put another metal back into solution. Thirdly, when complexing agents are in the wastewater, they will inhibit metal hydroxide precipitation.

**Sulfide precipitation**

Sulfide precipitation is also an effective process for the treatment of toxic heavy metals ions. One of the primary advantages of using sulfides is that the solubility’s of the metal sulfide precipitates are dramatically lower than hydroxide precipitates and sulfide precipitates are not amphoteric. And hence, the sulfide precipitation process can achieve a high degree of metal removal over a broad pH range compared with hydroxide precipitation. Metal sulfide sludge also exhibit better thickening and dewatering characteristics than the corresponding metal hydroxide sludge’s.

The investigation was done of pyrite and synthetic iron sulfide to remove Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$. The mechanism governing the metal removal processes was determined as chemical precipitation at low pH (<3) due to H$_2$S generation and adsorption at high pH (3 to 6). Recently, new sulfide precipitation process has been developed based on sulfate-reducing bacteria (SRB). SRB oxidize simple organic compounds under anaerobic conditions and the SRB transform the sulfates into hydrogen sulfide where CH$_2$CH(OH)COOH stands for simple organic compounds. Hydrogen sulfide reacts with divalent soluble metals to form insoluble metal sulfides.
Some attractive findings were reported and developed an upflow fixed-bed SRB to monitor for the treatment of zinc-bearing wastewater [134]. They found that the reactor has a considerable capacity of completely reducing sulfates for initial concentrations up to 6000 mg l\(^{-1}\), completely removing soluble zinc for initial concentrations up to 400 mg l\(^{-1}\) and completely removing TOC for initial concentrations up to 1500 mg l\(^{-1}\). The possibility of using SRB for the treatment of an acid mine drainage was also studied. However, there are potential dangers in the use of sulfide precipitation process. Heavy metal ions and sulfide precipitants often in acid conditions can result in the evolution of toxic H\(_2\)S fumes. It is essential that this precipitation process be performed in a neutral or basic medium. Moreover, metal sulfide precipitation tends to form colloidal precipitates that cause some separation problems in either settling or filtration processes.

**Chemical precipitation combined with other methods**

Chemical precipitation has been shown to be successful in combination with other methods. Sulfide precipitation for reuse and recover heavy metal ions and employed nanofiltration as a second step were reported [104]. Results indicated sulfide precipitation was successful in reducing the metal content and nanofiltration yielded solutions capable to being directly reused in the plant. Electro-Fenton process and chemical precipitation to treat rayon industry wastewater to reduce its COD (2400 mg l\(^{-1}\)) and Zn\(^{2+}\) (32 mg l\(^{-1}\)) were used. Results revealed that approximately 88% COD was reduced using Electro-Fenton method and zinc removal (99 to 99.3%) was attained in the range of pH 9 to 10 using lime precipitation. There are some reports on chemical precipitation in combination with ion-exchange treatments. Ion exchange processes individually and then combining with chemical precipitation in removing nickel from wastewater streams from a rinse bath of aluminum parts were studied [199]. They found that the individual application of ion exchange led to the removal of nickel up to 74.8%, while using the combination of ion exchange and precipitation processes, higher removal from 94.2% to 98.3% was obtained. Besides, treating acid mine water by the precipitation of heavy metals with lime and sulfides, followed by ion exchange was also reported [91].
Heavy metal chelating precipitation

Conventional chemical precipitation processes have many limitations and it is difficult to meet the increasingly stringent environmental regulations by application of conventional precipitation processes to treat the heavy metal wastewaters, especially containing coordinated agents. As an alternative, many companies use chelating precipitants to precipitate heavy metals from aqueous systems. The effectiveness of three widely used commercial heavy metal precipitants, trimercaptotriazine, potassium/sodium thiocarbonate and sodiumdimethylidithiocarbamate was reviewed and examined [161]. Since commercial heavy metal precipitants today either lack the necessary binding sites or pose too many environmental risks to be safely utilized, there is a definite need for new and more effective precipitants to be synthesized to meet the discharged requirements. Dithiocarbamate-type supramolecular heavy metal precipitants, N,N0-bis-(dithiocarboxy)piperazine (BDP) and 1,3,5-hexahydrotriazinedithiocarbamate (HTDC) were employed in treating complex heavy metal wastewater [96]. Results indicated that both BDP and HTDC could effectively reduce heavy metal ions in wastewater to much lower than 0.5 mg/l. The xanthate process has also been shown to be an effective method for heavy metal removal from contaminated water. Potassium ethyl xanthate was employed to remove copper ions from wastewater [56] and results showed that ethyl xanthate was suitable for the treatment of copper-containing wastewater over a wide copper concentration range (50, 100, 500 and 1000 mg/l) to the level that meets the Taiwan EPA’s effluent regulations (3.0 mg/l). A new organic heavy metalchelatordipropyl dithiophosphate was developed. The chelator can remove the concentration of lead, cadmium, copper and mercury being 200 mg/l at pH 3 to 6 up to over 99.9% and the heavy metal concentrations in the wastewater after treatment are less than 1, 0.1, 0.5 and 0.05 mg/l, respectively [283].

2.2.2. Ion exchange

Ion-exchange processes have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics [121]. Ion-exchange resin, either synthetic or natural solidresin, has the specific ability to
exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution [22].

The most common cation exchangers are strongly acidic resins with sulfonic acid groups (eSO₃H) and weakly acid resins with carboxylic acid groups (eCOOH). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. As the solution containing heavy metal passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin. The uptake of heavy metal ions by ion-exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time [101]. Ionic charge also plays an important role in ion-exchange process. The influence of ionic charge on the removal of Ce⁴⁺, Fe³⁺, Pb²⁺ from aqueous systems by cation-exchange resin purolite C100 was tested [2]. They found that the metal ions adsorption sequence can be given as Ce⁴⁺ > Fe³⁺ > Pb²⁺. Similar results for Co²⁺, Ni²⁺ and Cr²⁺ on an Amberlite IRN-77 cation exchange resin were previously obtained [121].

Besides synthetic resins, natural zeolites, naturally occurring silicate minerals have been widely used to remove heavy metal from aqueous solutions due to their low cost and high abundance. Many researchers have demonstrated that zeolites exhibit good cation-exchange capacities for heavy metal ions under different experimental conditions [172, 187, 239]. Clinoptilolite is one of the most frequently studied natural zeolites that have received extensive attention due to its selectivity for heavy metals. Recently, some researchers reported that the surface of clinoptilolite loaded with amorphous Fe-oxide species would significantly improve the exchange capacity of clinoptilolite [72, 76]. Clinoptilolite Fe system was employed to simultaneously remove Cu, Mn and Zn from drinking water [76]. He found that the system has very large metal adsorption capacity and for most of the cases the treated water samples were suitable for human consumption or agricultural use [76]. Though there are many reports on the use of zeolites and montmorillonites as ion-exchange resin to remove heavy metal, they are
limited at present compared with the synthetic resins. And the application of zeolites is on the laboratory experiments scale.

2.2.3. Membrane technologies

Membrane filtration technologies with different types of membranes show great promise for heavy metal removal for their high efficiency, easy operation and space saving. The membrane processes used to remove metals from the wastewater are ultra filtration, reverse osmosis, nano filtration and electro dialysis.

**Ultra filtration**

Ultra filtration (UF) is a membrane technique working at low transmembrane pressures for the removal of dissolved and colloidal material. Since the pore sizes of UF membranes are larger than dissolved metal ions in the form of hydrated ions or as low molecular weight complexes, these ions would pass easily through UF membranes. To obtain high removal efficiency of metal ions, the micellar enhanced ultra filtration (MEUF) and polymer enhanced ultra filtration (PEUF) was proposed.

MEUF was first introduced by Scamehorn et al. in the 1980s for the removal of dissolved organic compounds and multivalent metal ions from aqueous streams. MEUF has been proven to be an effective separation technique to remove metal ions from wastewater. This separation technique is based on the addition of surfactants to wastewater. When the concentration of surfactants in aqueous solutions is beyond the critical micelle concentration (CMC), the surfactant molecules will aggregate into micelles that can bind metal ions to form large metal-surfactant structures. The micelles containing metal ions can be retained by a UF membrane with pore sizes smaller than micelle sizes, whereas the untrapped species readily pass through the UF membrane. To obtain the highest retentions, surfactants of electric charge opposite to that of the ions to be removed have to be used. Sodium dodecyl sulfate (SDS), an anionic surfactant, is often selected for the effective removal of heavy metal ions in MEUF.

Metal removal efficiency by MEUF depends on the characteristics and concentrations of the metals and surfactants, solution pH, ionic strength and parameters related to membrane operation. The investigation for the removal
of zinc from synthetic wastewater by MEUF using SDS. They found that rejection coefficients up to 99% were achieved when the surfactant to metal molar ratio (S/M) was above 5. MEUF was used to remove Cd\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) from synthetic water using two anionic surfactants [218]. SDS and linear alkylbenzene sulfonate (LAS) in a lab-scale membrane system. The molar concentration ratio of the surfactant to metal is higher than 5 in all the experiments. When the initial SDS concentration was below the CMC, metal retention higher than 90% was unexpectedly obtained, except for Ni\(^{2+}\). Moreover, it was shown that complete removal of metal ions, except for Ni\(^{2+}\), could be achieved at an LAS concentration below CMC.

The retentate is the concentrated solution of surfactants and heavy metals retained by membrane. Since the surfactant may account for a large portion of operating costs, it is essential to recover and reuse the surfactant as economically as feasible. And if the surfactant and heavy metals are not disposed, they will cause secondary pollution. Chelation followed by UF and acidification followed by UF was tested for the separation of Cd\(^{2+}\) or Zn\(^{2+}\) from SDS micelles in simulated retentate solution of MEUF and the reuse of SDS [147]. In the method using chelating agents, EDTA at pH 4.4 was the best for separating heavy metal ions (90.1% for Cd\(^{2+}\), 87.1% for Zn\(^{2+}\)) and recovering SDS (65.5% for Cd\(^{2+}\), 68.5% for Zn\(^{2+}\)). With the reclaimed SDS in MEUF, the removal efficiencies of heavy metal ions were 90.3% for Cd\(^{2+}\), 89.6% for Zn\(^{2+}\). In the method using acid agents, H\(_2\)SO\(_4\) at pH 1.0 was the best for separating heavy metal ions (98.0% for Cd\(^{2+}\), 96.1% for Zn\(^{2+}\)) and recovering SDS (58.1% for Cd\(^{2+}\), 54.3% for Zn\(^{2+}\)). The efficiencies of reclaimed SDS were 88.1% for removing Cd\(^{2+}\) and 87.8% for removing Zn\(^{2+}\) in MEUF PEUF was also been proposed as a feasible method to separate a great variety of metal ions from aqueous streams. PEUF uses water-soluble polymer to complex metallic ions and form a macromolecular, having a higher molecular weight than the molecular weight cut off of the membrane. The macromolecular will be retained when they are pumped through UF membrane. After that, retentate can be treated in order to recover metallic ions and to reuse polymeric agent. The main concern of the previous PEUF studies was to find suitable polymers to achieve complexation with metal ions. Complexing
agents such as polyacrylic acid (PAA) [140], polyethyleneimine (PEI), [26] diethylaminoethyl cellulose and humic acid etc., have been proven to achieve selective separation and recovery of heavy metals with low energy requirements.

The main parameters affecting PEUF are metal and polymer type, the ratio of metal to polymer, pH and existence of other metal ions in the solution. PEI was used as a polymer to study the complexation ultra filtration process in the selective removal of Cu(II) from Ni(II) contained in aqueous media [170]. Preliminary tests showed that optimal chemical conditions for Cu(II) and Ni(II) complexation by the PEI were pH > 6.0 and 8.0, respectively, and polymer/metal weight ratio of 3.0 and 6.0, respectively. The removal of chromium species from aqueous dilute solutions using PEUF process by three water-soluble polymers, namely chitosan, PEI and pectin was investigated [26]. High rejections approaching 100% for Cr(III) were obtained at pH higher than 7 for the three tested polymers. The advantages of PEUF include high removal efficiency, high binding selectivity and highly concentrated metal concentrates for reuse, etc.

**Reverse osmosis**

The reverse osmosis (RO) process uses a semi-permeable membrane, allowing the fluid that is being purified to pass through it, while rejecting the contaminants. RO is one of the techniques able to remove a wide range of dissolved species from water. It accounts for more than 20% of the world’s desalination capacity [223]. RO is an increasingly popular wastewater treatment option in chemical and environmental engineering. Using appropriate RO systems to remove heavy metals have been investigated, but these have yet to be widely applied. Cu$^{2+}$ and Ni$^{2+}$ ions were successfully removed by the RO process and the rejection efficiency of the two ions increased up to 99.5% by using Na 2EDTA [169]. A pilot-scale membrane bioreactor system in combination with RO was applied and they found heavy metal removal efficiencies were very high [79]. The major drawback of RO is the high power consumption due to the pumping pressures, and the restoration of the membranes.
Nanofiltration

Nanofiltration (NF) is the intermediate process between UF and RO. NF is a promising technology for the rejection of heavy metal ions such as nickel [175], chromium [177], copper [9, 70] and arsenic [85, 93] from wastewater. NF process benefits from ease of operation, reliability and comparatively low energy consumption as well as high efficiency of pollutant removal. The removal of pentavalent arsenic from synthetic water by two commercial NF membrane (NF90 and N30F) was studied [93]. They found that an increase of pH and a decrease of operating temperature and as feed concentration led to higher as removal for both membranes. Among the parameters affecting the as rejection, feed concentration plays a key role for the production of a permeate stream. In recent years, a lot of work was devoted for the removal of heavy metal ions using NF membrane. Reports are the reapplication of a thin-film composite polyamide NF membrane for the rejection of nickel ions from aqueous wastewater [175]. The maximum observed rejection of nickel is found to be 98% and 92% for an initial feed concentration of 5 and 250 mg/l, respectively. And they investigated the binary heavy metals (cadmium and nickel) separation capability of a commercial NF membrane from aqueous solutions. The maximum observed solute rejection of nickel and cadmium ions is 98.94% and 82.69%, respectively, for an initial feed concentration of 5 mg/l. There are many reports on the removal of heavy metal by NF and RO membrane [175].

NF and RO were used to recover copper from process wastes [70]. The performance of different NF and RO membranes in treating the toxic metal effluent from metallurgical industry were studied [150]. They reported that the product water by both NF and RO desalination satisfied the State Reutilization Qualification, but NF would be more suitable for large-scale industrial practice. The recovery of silver from mining wastewaters using NF or RO after the silver is taken into solution as AgCN employing re-cyanidation and subsequent sedimentation and/or pre-filtration of wastewaters were investigated [133]. Silver recoveries achieved by hybrid cyanidation and membrane separation were 29 to 59% and 54 to 62% for NF and RO membranes, respectively.
2.2.4. Electrodialysis

Electrodialysis (ED) is another membrane process for the separation of ions across charged membranes from one solution to another using an electric field as the driving force. In most ED processes, ion-exchange membranes are used. The membranes are actually of two basic types: cation-exchange and anion-exchange membranes. This process has been widely used for the production of drinking and process water from brackish water and seawater, treatment of industrial effluents, recovery of useful materials from effluents and salt production [212]. ED has also proven a promising method in heavy metal wastewater treatment. A new working system was investigated for the removal of hexavalent chromium ions using a built ED pilot plant comprising a set of ion-exchange membranes. Results were satisfactory in meeting the maximum contamination level of 0.1 mg/l for chromium. The effectiveness of ED for the separation of Cu and Fe and water recovery from solutions in copper electrowinning operations was studied [67]. They found that ED proved very effective in the removal of Cu and Fe from the working solution. The separation of Cr(III) was studied from sodium ion by ED using modified cation-exchange membranes [142]. The effect of operating parameters on Pb²⁺ separation from wastewater using ED was studied [168]. The results showed that increasing voltage and temperature improved cell performance; however, the separation percentage decreased with an increasing flow rate. At concentrations of more than 500 mg/l, dependence of separation percentage on concentration diminished.

2.2.5. Coagulation and flocculation

Coagulation and flocculation followed by sedimentation and filtration is also employed to remove heavy metal from wastewaters. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Many coagulants are widely used in the conventional wastewater treatment processes such as aluminum, ferrous sulfate and ferric chloride, resulting in the effective removal of wastewater particulates and impurities by charge neutralization of particles and by enmeshment of the impurities on the formed amorphous metal hydroxide precipitates. The removal of heavy metal by coagulation of combined sewer overflow with two commercial coagulants, a
ferric chloride solution and a polyaluminium chloride (PAC) was investigated [219]. They found excellent heavy metal elimination was achieved within a narrow range of coagulant around optimum coagulant concentrations. Coagulation is one of the most important methods for wastewater treatment, but the main objects of coagulation are only the hydrophobic colloids and suspended particles.

In order to remove both soluble heavy metal and insoluble substances efficiently by coagulation, sodium xanthogenate group was grafted to polyethylenimine [54]. This new kind of coagulant was an amphoteric polyelectrolyte. When the pH of water sample is lower, the colloidal substances with negative charges can be coagulated by it, but the cationic Ni$^{2+}$ ion cannot be removed very well. When the pH of water sample is higher, the turbidity removal decreases, and the Ni$^{2+}$ removal increases. Flocculation is the action of polymers to form bridges between the flocs and bind the particles into large agglomerates or clumps. Once suspended particles are flocculated into larger particles, they can usually be removed or separated by filtration, straining or floatation.

Today many kinds of flocculants, such as PAC, polyferric sulfate (PFS) and polyacrylamide (PAM), are widely used in the treatment of wastewater, however, it is nearly impracticable to remove heavy metal very well from wastewater directly by these current flocculants. Macromolecule heavy metal flocculants is a new kind of flocculant. A macromolecule heavy metal flocculant (mercaptoacetyl chitosan) was prepared by reacting chitosan with mercaptoacetic acid [55]. They reported that this new flocculant could not only remove turbidity, but also remove heavy metals in wastewater.

Flocculants of Konjac-graft-poly (acrylamide)-co-sodium xanthate [78] and polyampholyte chitosan derivatives e N-carboxyethylated chitosans were also used to remove heavy metals. The research on flocculation by humid acid (HA) binding heavy metal is also investigated. The enhanced removal of heavy metal ions from solution, such as Pb$^{2+}$ and Zn$^{2+}$, was studied by binding the ions to HA and then coagulating and flocculating with the cationic polyelectrolyte polydiallyl dimethylammonium chloride (Poly- DADMAC) [110]. The removal of bound metal ions was found to increase with the extent of
coagulation flocculation of the HA by Poly DADMAC. Generally, metal-HA complexes are removed from a solution by polyelectrolyte flocculation, followed by centrifugation or filtration. Recently, a flocculation technique using a thermo sensitive polymer to remove undesirable heavy metals and humid substances, and this technique is free from centrifugation and filtration was proposed [243]. Besides, a new commercial tannin-based flocculent has been reported to remove Zn\(^{2+}\), Ni\(^{2+}\) and Cu\(^{2+}\) by coagulation flocculation process [113].

Generally, coagulation flocculation cannot treat the heavy metal wastewater completely [54]. Therefore, coagulation flocculation must be followed by other treatment techniques. Precipitation, coagulation and flocculation processes using ferric chloride to remove tungsten from industrial wastewater was employed [203]. Tungsten removal was found to be most efficient (98 to 99%) in acidic conditions (pH < 6). Spontaneous reduction coagulation process using micro-alloyed aluminum composite in a laboratory semi flow system to treat model heavy metal wastewater was employed [41]. The residual concentrations of metals were at admissible levels after only 20 minutes of treatment.

2.2.6. Flotation

Flotation has nowadays found extensive use in wastewater treatment. Flotation has been employed to separate heavy metal from a liquid phase using bubble attachment, originated in mineral processing. Dissolved air flotation (DAF), ion flotation and precipitation flotation are the main flotation processes for the removal of metal ions from solution. DAF is to allow micro-bubbles of air to attach to the suspended particles in the water, developing agglomerates with lower density than water, causing the flocs to rise through the water and accumulating at the surface where they can be removed as sludge [156].

Ion flotation has been shown a promising method for the removal of heavy metal ions from wastewaters. The process of ion flotation is based on imparting the ionic metal species in wastewaters hydrophobic by use of surfactants and subsequent removal of these hydrophobic species by air bubbles [204]. The potential of ion flotation to remove cadmium, lead and
copper from dilute aqueous solution with a plant-derived biosurfactant tea saponin was investigated. The maximum removal of Pb^{2+}, Cu^{2+} and Cd^{2+} can reach 89.95%, 81.13% and 71.17%, respectively, when the ratio of collector to metal was 3:1. Ion flotation to remove Cu^{2+}, Zn^{2+}, Cr^{2+} and Ag^{+} from wastewaters was implemented [204]. SDS and hexadecyltrimethyl ammonium bromide were used as collectors. Ethanol and methyl isobutyl carbinol were used as frothers. Metal removal reached about 74% under optimum conditions at low pH. At basic pH it became as high as 90%, probably due to the contribution from the flotation of metal precipitates.

Precipitate flotation process is another alternative of flotation method, based on the formation of precipitate and subsequent removal by attachment to air bubbles. Depending on the concentration of the metal solution, the precipitation may proceed via metal hydroxide formation or as a salt with a specific anion (sulfide, carbonate, etc.) [50]. The removal of Cr(III) by precipitate flotation from dilute aqueous solutions, using SDS as anionic collector and ethanol as further was investigated at laboratory scale [164]. The results showed that a 96.2% maximum removal was achieved at pH around 8.0.

2.2.7. Electrochemical treatment

Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state. Electrochemical wastewater technologies involve relatively large capital investment and the expensive electricity supply, so they haven’t been widely applied. However, with the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades [272]. The established technologies, electro coagulation, electro flotation, and electrode position were also examined.

Electro coagulation (EC) involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from aluminum or iron electrodes [59]. The metal ion generation takes place at the anode, and hydrogen gas is released from the cathode. The hydrogen gas can help to float the flocculated particles out of the water [59]. The performance of an EC
system was studied with aluminum electrodes for removing Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Ag$^{+}$ and Cr$_{2}$O$_{7}$$^{2-}$ was studied [112]. Initial concentrations from 50 to 5000 mg/l$^{-1}$ Zn, Cu, Ni and Ag did not influence the removal rates, whereas higher initial concentrations caused higher removal rates of Cr, Zn, Cu, Ni and Ag ions were hydrolyzed and co-precipitated as hydroxides [112]. Cr(VI) was proposed to be reduced first to Cr(III) at the cathode before precipitating as hydroxide.[122] The treatability of a metal plating wastewater containing complex metals originating from the nickel and zinc plating process by accusing stainless steel electrodes experimentally investigated. Their study demonstrated that the highest TOC abatement (66%) as well as nickel and zinc removals (100%) were achieved with an applied current density of 9.0 mA cm$^{-2}$ at the original electrolyte (chloride) concentration and original pH of the composite sample used. EC was also used to evaluate the treatment of synthetic solutions containing Hg$^{2+}$ of concentration 2-5 M [182].

The removal efficiency was above 99.9% when the distance between the electrodes was 3 cm, the current density ranging from 2.5 to 3.125 Adm$^{-2}$ and pH of the Hg$^{2+}$ solutions from 3.0 to 7.0. [186] studied the performance of EC to remove hexavalent chromium having a high Cr(VI) concentration of 1470 mg/l$^{-1}$. The optimum conditions for 100% Cr(VI) removal were established as 7.4 A applied electric current, 33.6 mM electrolyte (NaCl) concentration and 70 min application time. Besides, EC has been employed to remove Mn$^{2+}$, As(V), Mn$^{2+}$, and Ni$^{2+}$, etc. floats pollutants to the surface of a water body by tiny bubbles of hydrogen and oxygen gases generated from water electrolysis. EF has wide range applications in heavy metals removal from industrial wastewater.

The clarification of wastewater by using the EF technique with aluminum electrodes and the application of the optimized parameters on the separation of some heavy metal ions such as iron, nickel, copper, zinc, lead and cadmium was studied [34]. Their study demonstrated that the metal removal rate reached 99%. EF with iron electrodes hybrid with filter paper, micro and ultra-filtration bench scale tests were performed to obtain high removal efficiency of nickel with and without the introduction of external oxygen [237]. Research results indicated that with the hybridization of EF
without aeration followed by microfiltration and aeration-enhanced EF followed by settling and mechanical filtration, the residual nickel and iron could meet the discharge standard of metal finishing industry.

Electrode position has been usually applied for the recovery of metals from wastewater. It is a “clean” technology with no presence of the permanent residues for the separation of heavy metal [119]. The electrode position is an applicable method for the recovery of metals under appropriate conditions [188]. They investigated the electrolytic recovery of metals from aqueous solutions containing complexing chelating agents such as EDTA, nitrilotriacetic acid and citrate in a two-chamber cell separating with a commercial cation exchange membrane. The results showed that least value of recovery of metal was approximately 40% and this value increased due to the type of the experiments up to 90% for copper. Electrode position in conjunction with ultrasound to reclaim EDTA copper wastewater was studied [53].

They found that the technique can effectively remove copper (95.6%) and decompose EDTA (84% COD removal) from wastewater. The electrode position of copper and lead ions onto palm shell AC electrodes were presented [119]. Besides, recovery of Cd and Ni by electrode position was investigated [286].

Although all the heavy metal wastewater treatment techniques can be employed to remove heavy metals, they have their inherent advantages and limitations. Heavy metals removal from aqueous solutions has been traditionally carried out by chemical precipitation for its simplicity process and inexpensive capital cost. However, chemical precipitation is usually adapted to treat high concentration wastewater containing heavy metal ions and it is ineffective when metal ion concentration is low. Chemical precipitation is not economical and can produce large amount of sludge to be treated with great difficulties. Ion exchange has been widely applied for the removal of heavy metal from wastewater. However, ion-exchange resins must be regenerated by chemical reagents when they are exhausted and the regeneration can cause serious secondary pollution. And it is expensive, especially when
treating a large amount of wastewater containing heavy metal in low concentration, so they cannot be used at large scale.

Adsorption is a recognized method for the removal of heavy metals from low concentration wastewater containing heavy metal. The high cost of AC limits its use in adsorption. Many varieties of low-cost adsorbents have been developed and tested to remove heavy metal ions. However, the adsorption efficiency depends on the type of adsorbents. Biosorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising for the removal of heavy metal from wastewater. Membrane filtration technology can remove heavy metal ions with high efficiency, but its problems such as high cost, process complexity, membrane fouling and low permeate flux have limited their use in heavy metal removal. Using coagulation flocculation heavy metal wastewater treatment technique, the produced sludge has good sludge settling and dewatering characteristics. But this method involves chemical consumption and increased sludge volume generation. Flotation offers several advantages over the more conventional methods, such as high metal selectivity, high removal efficiency, high overflow rates, low detention periods, low operating cost and production of more concentrated sludge [211].

But the disadvantages involve high initial capital cost, high maintenance and operation costs. Electrochemical heavy metal wastewater treatment techniques are regarded as rapid and well-controlled that require fewer chemicals, provide good reduction yields and produce less sludge. However, electrochemical technologies involving high initial capital investment and the expensive electricity supply, this restricts its development. Although all above techniques can be employed for the treatment of heavy metal wastewater, it is important to mention that the selection of the most suitable treatment techniques depends on the initial metal concentration, the component of the wastewater, capital investment and operational cost, plant flexibility and reliability and environmental impacts [137].
<table>
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<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<td>1.</td>
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<td>Simple Inexpensive Most of metals can be removed</td>
<td>Large amounts of sludge produced Disposal problems</td>
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<td>2.</td>
<td>Chemical coagulation</td>
<td>Sludge settling Dewatering</td>
<td>High cost Large consumption f chemicals</td>
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<td>3.</td>
<td>Ion-exchange</td>
<td>Sludge settling Dewatering</td>
<td>High cost Less number of metal ions removed</td>
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<td>4.</td>
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<td>High capital cost High running cost Initial solution pH and Current density</td>
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<td>5.</td>
<td>Adsorption Using activated carbon</td>
<td>Most of metals can be removed High efficiency (&gt;99%)</td>
<td>Cost of activated carbon No regeneration Performance depends upon adsorbent</td>
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<td>6.</td>
<td>Using natural zeolite</td>
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<td>7.</td>
<td>Membrane process and ultrafiltration</td>
<td>Less solid waste produced Less chemical consumption High efficiency (&gt;95% for single metal)</td>
<td>High initial and running cost Low flow rates Removal (%) decreases with the presence of other metals</td>
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</table>
2.3. Biosorption

Biosorption is rather difficult to define because many mechanisms may contribute to the overall process depending on the substance to be sorbed, the biosorbent used, environmental factors and the presence or absence of metabolic processes in the case of living organisms. Biosorption may be simply defined as the removal of substances from solution by biological material. Such substances can be organic and inorganic and in soluble or insoluble forms.

The 'bio' prefix denotes the involvement of a biological entity, i.e. living organism, component or product produced or derived from a living organism, exactly as in other terms like biotechnology, bioengineering, and bioprocessing. Coupling of 'bio' to a physico-chemical expression like 'sorption' also denotes the involvement of living organisms but does not necessarily mean that the 'sorption' process is somehow different to sorption in abiotic systems [99].

Biosorption is a physico-chemical process and includes such mechanisms as absorption, adsorption, ion exchange, surface complexation and precipitation. It is a property of living and dead biomass (as well as excreted and derived products): metabolic processes in living organisms may affect physico-chemical biosorption mechanisms, as well as pollutant bioavailability, chemical speciation and accumulation or transformation by metabolism-dependent properties.

The biosorption process involves a solid phase (sorbent or biosorbent; usually a biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, a metal ion). Due to higher affinity of the sorbent for the sorbate species the latter is attracted and bound with different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. While there is a preponderance of solute (sorbate) molecules in the solution, there are none in the sorbent particle to start with. This imbalance between the two environments creates a driving force for the solute species. The heavy metals adsorb on the surface of
biomass thus, the biosorbent becomes enriched with metal ions in the sorbate. [19]

2.3.1. Initial History of Biosorption

Biosorption has received considerable attention as in recent years. As early as 1935, Adams and Holmes (1935) used the tannin resins of black wattle bark (A. mollissima) to bind calcium and magnesium ions from waste water on to woody fibers. It was their work that pioneered the field of ion exchange which eventually leads to the field of biosorption. Although the ability of living microorganisms to take up metals from aqueous solution was investigated as early as 18th and 19th centuries [167], it is only during the last three decades that living or non-living microorganisms have been used as adsorbents for removal and recovery of materials from aqueous solutions. The earliest technological applications of biosorption techniques involved sewage and waste treatment [248]. It was also investigated for use in renovating wastewater generated by the chemical industry [235]. The first patent for a biosorption apparatus used for biological treatment of wastewater was registered by the Ames Crosta Mills & Company Ltd. in 1973 [23].

Scientists in life sciences primarily focused on the toxicological effects and accumulation of heavy metals in microorganisms, while environmental scientists and engineers used this capability of microorganisms as a means of monitoring heavy metal pollution, as well as, for removal/recovery of metals from metal-bearing wastewaters [173]. The first patent on the use of biosorption technology for removing uranium or thorium ions from aqueous suspension/solution was granted to B. Volesky and M. Tsezos in 1982 [264].

Goodman and Roberts (1971) reported the practical use of biosorption technology for monitoring trace heavy metals in the environment [105]. As the emission standards tighten the common ones are becoming progressively more inadequate or prohibitively costly for use of wastewater treatment. Better and effective metal-removal technologies are invariably more costly and often just not feasible for that purpose. The search is on for efficient and particularly cost-effective remedies. Biosorption promises to fulfill the requirements. Its overall performance and process application modes justify a comparison with the ion exchange technology. [260]
2.3.2. Advantages of biosorption

The interest in biological substrates for the removal of toxic metal ions has grown as research continues to display the increasing benefits of this treatment process. The advantages of biosorption process over conventional methods for the removal of metals from dilute solutions (such as oxidation and reduction, chemical precipitation, filtration, electrochemical treatment, evaporation, ion-exchange resins, and reverse osmosis processes) include:

- High efficiency of removal from dilute metal solutions- biosorption is particularly suited for the purification of wastewaters with a metal concentration of about 1-100 ppm [222];
- Potential for metal recovery-accelerating depletion of natural resources and rising prices of metals make metal recycling very attractive;
- Low cost-price of biosorbents range can be an order of magnitude cheaper (one-tenth) than ion exchange resins [259];
- No sludge generation-other processes, namely precipitation, produce sludge or other secondary contamination [259];
- Abundance of material-many effective biosorbents are either abundant in nature or cheap waste products of other industries [82];
- Regenerative properties- the metals may be desorbed from the biosorbent that may then be reused with a minimal decrease in sorption performance [72];
- Metal selectivity potential-the metal sorbing capabilities of different types of biomass can be vary in selectivity for different metals. The selection may be achieved during either the adsorption stage or the desorption stage [259].

2.3.3. Choice of metal for biosorption

The appropriate selection of metals for biosorption studies is dependent on the angle of interest and the impact of different metals, on the basis of which they would be divided into four major categories; toxic heavy metals, strategic metals, precious metals and radio nuclides. In terms of environmental threats, main categories of interest for removal from the environment and/or from point source effluent discharges are toxic metals and radio nuclides. Apart from toxicological criteria, the interest in specific metals...
may also be based on how representative their behaviour may be in terms of eventual generalization of results of studying their biosorbent uptake. The toxicity and interesting solution chemistry of elements such as chromium, arsenic and selenium make them interesting to study. Strategic and precious metals though not environmentally threatening are important from their recovery point of view. [5]

2.3.4. Process factors influencing biosorption

For the industrial application of biosorption technology for pollutant removal, it is very important to investigate the removal efficiency of a given biosorbent for the target pollutant. Pollutant uptake can involve different types of biosorption processes that will be affected by various physical and chemical factors, and these factors will determine the overall biosorption performance of a given biosorbent, (i.e. its uptake rate, its specificity for the target, and the quantity of target removed). For this reason, the first step of almost all research has been to examine the individual and/or cooperative effect(s) of various factors on biosorption [52, 69, 154, 165, 167].

In the case of batch biosorption processes for removing adsorptive pollutants such as ionic metals or dyes, the important factors include solution pH, temperature, ionic strength, initial pollutant concentration, biosorbent dosage, biosorbent size, agitation speed, and also the coexistence of other pollutants. Batch experiments usually focus on the study of factors influencing biosorption, which are important in the evaluation of the full biosorption potential of any biomaterial. The important factors include:

The solution pH usually plays a major role in biosorption, and seems to affect the solution chemistry of metals/dyes and the activity of the functional groups of the biomass. For metals, the pH strongly influences the speciation and biosorption availability of the metal ions [87, 285]. At higher solution pH, the solubility of metal complexes decreases sufficiently allowing precipitation, which may complicate the sorption process. The activity of binding sites can also be altered by adjustment of the pH. For instance, during the biosorption of metal ions by bacterial biomass, pH 3 to 6 has been found favourable for biosorption due to the negatively charged carboxyl groups (pKₐ:3–5), which are responsible for the binding metal cations via ion exchange mechanism. In
the case of the biosorption of dyes, different dye classes require different pH ranges. For instance, basic dyes require alkaline or neutral conditions [89]; whereas, reactive dyes demand strong acidic conditions for their optimum biosorption [157].

Temperature seems to affect biosorption only to a lesser extent within the range from 20 to 35°C [252]. Higher temperatures usually enhance sorption due to the increased surface activity and kinetic energy of the solute [215, 255]; however, physical damage to the biosorbent can be expected at higher temperatures. Due to the exothermic nature of some adsorption processes, an increase in temperature has been found to reduce the biosorption capacity of the biomass. It is always desirable to conduct/evaluate biosorption at room temperature, as this condition is easy to replicate.

Ionic strength, another important parameter in biosorption is the ionic strength, which influences the adsorption of solute to the biomass surface [42, 71]. The effect of ionic strength may be ascribed to the competition between ions, changes in the metal activity, or in the properties of the electrical double layer. When two phases, e.g. biomass surface and solute in aqueous solution are in contact, they are bound to be surrounded by an electrical double layer owing to electrostatic interaction. Thus, adsorption decreases with increase in ionic strength [75]. Some inorganic ions, such as chloride, may form complexes with some metal ions and therefore, affect the sorption process.

Dose of a biosorbent strongly influences the extent of biosorption. In many instances, lower biosorbent dosages yield higher uptakes and lower percentage removal efficiencies [13, 254]. An increase in the biomass concentration generally increases the amount of solute biosorbed, due to the increased surface area of the biosorbent, which in turn increases the number of binding sites [86]. Conversely, the quantity of biosorbed solute per unit weight of biosorbent decrease with increasing biosorbent dosage, which may be due to the complex interaction of several factors. An important factor at high sorbent dosages is that the available solute is insufficient to completely cover the available exchangeable sites on the biosorbent, usually resulting in low solute uptake [240]. Also, as suggested by [98], the interference between
binding sites due to increased biosorbent dosages cannot be overruled, as this will result in a low specific uptake. [98]

Size of particle of the biosorbent particle also plays a vital role in biosorption. Smaller sized particles have a higher surface area, which in turn favours biosorption and results in a shorter equilibration time. Simultaneously, a particle for biosorption should be sufficiently resilient to withstand the applicable pressures and extreme conditions applied during regeneration cycles [259]. Therefore, preliminary experiments are mandatory to decide the suitable size of a biosorbent. If a biosorbent is available in powdered form, such as industrial waste, efforts should be made to improve the mechanical strength, such as granulation, for its effective use in biosorption columns [256].

The initial solute concentration seems to have impact on biosorption, with a higher concentration resulting in a high solute uptake [38, 114, 115]. This is because at lower initial solute concentrations, the ratio of the initial moles of solute to the available surface area is low; subsequently, the fractional sorption becomes independent of the initial concentration. However, at higher concentrations, the sites available for sorption become fewer compared to the moles of solute present and; hence, the removal of solute is strongly dependent upon the initial solute concentration. It is always necessary to identify the maximum saturation potential of a biosorbent, for which experiments should be conducted at the highest possible initial solute concentration. In some instances, external film diffusion can influence the rate of a biosorption process. With appropriate agitation, this mass transfer resistance can be minimized. When increasing the agitation rate, the diffusion rate of a solute from the bulk liquid to the liquid boundary layer surrounding particles becomes higher due to the enhanced turbulence and the decrease in the thickness of the liquid boundary layer [88]. Under these conditions, the value of the external diffusion coefficient becomes larger [225]. Finally, at higher agitation rates, the boundary layer becomes very thin, which usually enhances the rate at which a solute diffuse through the boundary layer. [256]
2.3.5. Mechanisms of biosorption

The complex structure of microorganisms implies that there are many ways for the metal to be taken up by the microbial cell. The biosorption mechanisms are various and are not fully understood. They may be classified according to various criteria. According to the dependence on the cell's metabolism, biosorption mechanisms can be divided into: metabolism dependent and non-metabolism dependent. According to the location where the metal removed from solution is found, biosorption can be classified as: Extra cellular accumulation/ precipitation Cell surface sorption/ precipitation and Intracellular accumulation.

Transport of the metal across the cell membrane yields intracellular accumulation, which is dependent on the cell's metabolism. This means that this kind of biosorption may take place only with viable cells. It is often associated with an active defense system of the microorganism, which reacts in the presence of toxic metal [5]. During non-metabolism dependent biosorption, metal uptake is by physico-chemical interaction between the metal and the functional groups present on the microbial cell surface. This is based on physical adsorption, ion exchange and chemical sorption, which is not dependent on the cells' metabolism. Cell walls of microbial biomass, mainly composed of polysaccharides, proteins and lipids have abundant metal binding groups such as carboxyl, sulphate, phosphate and amino groups. This type of biosorption, i.e., non-metabolism dependent is relatively rapid and can be reversible [139]. In the case of precipitation, the metal uptake may take place both in the solution and on the cell surface [85]. Further, it may be dependent on the cell's metabolism if, in the presence of toxic metals the microorganism produces compounds that favour the precipitation process. Precipitation may not be dependent on the cells' metabolism, if it occurs after a chemical interaction between the metal and cell surface.

2.3.6. Biosorption in the environment and in established waste treatment

In natural systems, bioavailability of nutrients, including essential metals, and pollutants is determined by interactions with environmental components. In terrestrial and aquatic ecosystems, such components include clay and other minerals, humic substances, soil colloidal materials, biogenic...
debris and exudates and living organisms. Sorption is one of the most important reactions that influence bioavailability, and therefore biosorption must also have a role to play within the spectrum of sorptive interactions with environmental components. These will include influencing distribution of substances between aqueous solution and particulate matter (including microorganisms) and their transport through environmental compartments and ultimate fate, e.g. settling in ocean sediments. [99]

Biosorptive processes may be a component of varying significance in any form of primary or secondary biological treatment process for aqueous waters and process streams including domestic, municipal and industrial wastes and in some circumstances, solid wastes. Sewage treatment, activated sludge plants, biofilters, biofilm reactors, fixed and suspended film systems, lagoon treatments, stream meanders, nitrification and denitrification treatments, biological phosphate removal processes, wetlands and reed-bed technologies, composting, in situ and ex situ bioremediation processes all rely on the activities of microorganisms to break down organic substances. Many wastes contain metals as well as organics and therefore biosorption of metals and related materials may also play a part in the overall process. The significance of such a role is difficult to establish but it may be significant in some cases, the problem of metal-laden sewage disposal is well known. In biological treatment processes, a clear advantage is that metabolic activities contribute to the degradation of organic materials. Some examples have been described where organic and inorganic transformations are closely linked to biosorptive removal, e.g. rotating biological contactors to treat dilute metal-containing mine waste streams. [98, 99]

2.3.7. Potential applications for biosorption

The potential application for biosorption appears to be enormous. While the high cost of the ion exchange process limits its application (as demonstrated by the huge amount of untreated effluents still released), the cost advantage of biosorption technology would guarantee a strong penetration of the large market of heavy metal polluting industries. It can easily be envisaged that cheaper biosorbents would open up new, particularly environmental, markets so far non-accessible to ion exchange resins because
of their excessive costs which make them prohibitive for clean-up operation applications.

These considerations clearly demonstrate the economic feasibility and potential of the biosorption process for heavy metal removal/recovery purposes. It should be pointed out that there is a potential added benefit of metal-recovery as an additional source of revenue generated by a water treatment that must be carried out anyway (from a regulatory and environmental point of view). This cost reduction applies to “cheap” metal as well as “expensive” metal no matter what the economic indices may be [260]. Biosorption is particularly economical and competitive for environmental applications in detoxifying effluents from: metal plating and metal finishing operations, mining and ore processing operations, metal processing, battery and accumulator manufacturing operations, thermal power generation (coal-fired plants in particular) nuclear power generation.

2.3.8. Commercial applications of biosorption technology

In the early 1980s, the first patents appeared, claiming the use of specific microbial biomass types as biosorbents for wastewater treatment [246]. In the early 1990s, other biomaterials were developed and commercialized, including AlgaSORB™ (C. vulgaris), AMT-BIOCLAIM™ (Bacillus biomass) (MRA), Bio-fix, etc., prepared by immobilization technology [252, 267]. The immobilization of the microbial biomass seems indispensable for biosorption application and also can make use of traditional chemical engineering reactor configurations, such as up flow or down flow packed bed reactors, fluidized bed reactors. Also, some enterprises in North America were mentioned in developing the biosorption system. B. V. SORBEX, Inc. in Montreal, Canada, produced a series of biosorbents based on different types of biomaterial, including the algae S. natans, A. nodosum, Halimeda opuntia, Palmyra pamata, Chondrus crispus and C. vulgaris. The biosorbent was effective over a range of pH values and solution conditions can biosorb a wide range of metal ions.

The metal biosorption was not affected by calcium or magnesium, it was also not affected by organics, and can be regenerated easily. Advance Mineral Technologies Inc. in Golden, Colorado, developed a broad-range
metal-removal biosorbent based on Bacillus sp, but it stopped in late 1988 [267].

AlgaSORB™ was produced by Bio-recovery Systems Inc. in Las Cruces, New Mexico. The biosorbent based on immobilized Chlorella (a freshwater alga) in silica or polyacrylamide gels. It can efficiently remove metal ions from dilute solution of 1.0 to 100 mg·l⁻¹, thus may reduce the concentration to below 1.0 mg·l⁻¹ or lower. The heavy metal biosorption was not affected by light metals such as Ca²⁺ and Mg²⁺. The biosorbent resembles an ion-exchange resin and can undergo more than 100 biosorption–desorption cycles [138]. AMT-BIOCLAIM™ (Visa Tech Ltd.) comprises of Bacillus subtilis. It was treated with strong caustic solution, washed with water, and immobilized as porous balls onto polyethyleneimine and glutaraldehyde, which can efficiently remove metal ions [48, 252, 256]. Brierley introduced the production and application of this kind of Bacillus-based biosorbent. AMT- BIOCLAIM™ is able to accumulate gold, cadmium and zinc from cyanide solutions, and is therefore suitable for metal-finishing operations [28]. The biosorbent BIO-FIX is made up of a variety of biomasses, including Sphagnum peat moss, algae, yeast, bacteria, and/or aquatic flora immobilized in high density polysulfone. This biosorbent is selective for toxic heavy metals over that of alkaline earth metals [256]. U. S. Bureau of Mines (Golden, Colorado) produced the granular Bio-fix, which has been tested extensively for the treatment of acid minewast.

The results showed the Zn binding to the biosorbent BIO-FIX is about four fold higher than the ion exchange resins. The type of these systems employed is dependent on the amount of flow to be processed, its composition, its continuity, and the regeneration conditions. From the process of application point of view, the design and operation of the biosorption are similar to the established technologies for ion exchange resin or activated carbon adsorption. In these systems, pre-treatment of liquor may be required in some cases, depending on the suspended solids removal prior to biosorption. All the commercial biosorption enterprises, including both Biorecovery Systems and B. V. Sorbet, offer small “canisters” as flowthrough fixed-bed systems, as well as large-scale fluidized-bed, pulsed-bed systems,
multi-element large-scale treatment schemes capable of handling flows in excess of 100 m$^3$ d$^{-1}$ [267].

The treatment of wastewater was investigated in the flow rate ranging from 3.8 to 30 lmin$^{-1}$ using 79 kg of MRA, the result showed that the fluidized-bed contactors would offer optimum removal process using large amount of MRA [138]. The performance of the several biosorbents were summarized by [267], the major features are as follows: high versatility for wide-range of operational conditions, metal selectivity and not influenced by alkaline earth and common light metals, independent of concentration (for =10 ppm or =100 ppm), high tolerance to organics and convenient & effective regeneration [267]. Immobilized R. arrhizus biomass was tested for recovery of uranium from an ore bioleaching solution [252].

Two other commercialized biosorbents include 'MetaGeneR' and "RAHCO Bio-Beads". They are effective to remove metal ions from electroplating or mining waste streams. Information related to their industrial application is still limited although the extensive laboratory and field trials were carried out [28]. Metal biosorption by synthetic or biosynthetic chemicals was also investigated. For example, a kind of mercury-binding synthetic biosorbent, called Vitrokele™ 573, was prepared and used for mercury removal. This biosorbent is an insoluble composition comprising Hg binding groups in particular cysteine, covalently fixed to the surface of a suitable insoluble carrier. The basic formula of the group is carrier- R-Cys, where Cys is a cysteine residue, and R is a hydrocarbon chain. The batch and column tests demonstrated that mercury was efficiently removed from solution containing high concentration of sulfate and chloride. The biosorbent could be reused over multiple cycle’s.

Another Vitrokele™ product was iron-binding synthetic biosorbent. The common groups binding iron are hydroxamates and phenolate–catecholates, usually found in siderophore .The catecholate type Vitrokele™ was tested in a column containing 600 μM radioactive iron, cobalt, sodium and cadmium. The Vitrokele™ showed good affinity for Fe, but poor affinity for Co and no affinity for Na or Cd. Unlike the commercial ionexchange resins, the Vitrokele™ could remove trace amounts of iron from artificial seawater in the presence of high
concentration of other cations. It was not interfered by other cations and was not saturated quickly [273].

Biosorption of metal ions and organics from industrial wastewater on full-scale was mainly focused on the biosorbent of peat during the past decades. Some peat on-site wastewater treatment systems for ion removal were operated in Maine, Alaska, Canada, and Ireland. The peat was regarded as utilizable and disposable. With the emphasis on using readily renewable biosorbents, peat-involving systems become much more engineered and much more specific, such as membrane-media extraction process developed by Harrison Western Environmental Services Inc. of Lakewood, Colorado. The process used peat moss capsules and was able to effectively treat As, Cd, Pb, Ni, Se and other metals from several type of wastewater, including electroplating rinsewater, pulp and paper mill discharge, municipal wastewater and acid mine drainage. In order to meet the renewable demand, another alternative is to take a pure component in a load-regeneration cycle system. The cellulosic sago waste was more effective than peat for Pb removal [274]. Peat was regarded as the most successful and the rigorously scrutinized biosorbent in its natural state or in a modified form. Designs for large-scale peat-sorption processes are also available for application. However, the supply of peat is finite, and probably not the best biomaterial resource for commercialization. Thus, the development of other forms of biosorbents is essential. Three types of biomasses, including algae, fungi and waste biomass were suggested as potential biosorbents after predicting the future for biosorption application [94, 273, 274].

2.3.9. Biosorbent selection and assessment

The two types of investigations could help to examine a solid–liquid sorption system include equilibrium batch sorption tests and dynamic continuous-flow sorption studies. The Langmuir model and the Freundlich model are two widely accepted equilibrium adsorption isotherm models for single solute systems. $q_{\text{max}}$ is the maximum sorption capacity corresponding to complete monolayer coverage (mmol g$^{-1}$), $C_e$ (mmol l$^{-1}$) is the equilibrium solute concentration, and $b$ is the equilibrium constant related to the energy of sorption (or “affinity”) (l mmol$^{-1}$), $K_f$ and $n$ are the Freundlich constants related
to the adsorption capacity and intensity of the biosorbent, respectively. These parameters from the models could be used for comparing the biosorbents performances. The evaluation of sorption systems is based on the classical sorption isotherm derived from equilibrium batch contact experiments under the same environmental conditions (e.g. pH, temperature, ionic strength). A quantitative comparison of two different sorption systems can only be made at the same equilibrium (final, residual) concentration. Thus comparison at low equilibrium concentration $C_f$ (e.g., 10 mg l$^{-1}$) and another at high equilibrium concentration $C_f$ (e.g., 200 mg l$^{-1}$) are made in some biosorption screens.

The Langmuir isotherm model incorporates two easily interpretable constants: $q_{max}$ and $b$. Low values of $b$ are reflected in the steep initial slope of a sorption isotherm, indicating a desirable high affinity. Thus, for ‘good’ sorbents in general, one is looking for a high $q_{max}$ and a steep initial sorption isotherm slope (i.e. low $b$) \[135\]. Any other comparison may carry an inherent error. The comparison of sorbent performance based on ‘% removal’ (percent of metal removal) is an often-used criterion encountered in the literature. The authors strengthened that even if all experimental parameters are given, this criterion can only result in a qualitative, and relative comparison (better or worse performance) that is adequate only for material screening purposes. The presence of other ions in solution can complicate the evaluation of the sorption system to a large degree, depending on the way the new solute species interact with the sorbent and with the original one. Knowledge on these aspects may not be readily available. Appropriate and meaningful evaluation of a sorbent system with three or more metallic ions becomes even more complicated, if not impossible for all practical purposes." ‘% removal’ can only serve the purpose of crude orientation, such as a qualitative comparison, often used for quick and very approximate screening of biosorbent materials. To obtain the laboratory equilibrium sorption data, enough time must be allowed for the sorption system to reach equilibrium [271]. A simple preliminary sorption kinetics test should be performed to determine the exposure time necessary for the given sorbent particles to reach the equilibrium state (characterized by unchanging sorbate concentration in the solution) by using time based analyses. The evaluation of
equilibrium sorption performance needs to be supplemented by process-oriented studies of its kinetics and eventually by dynamic continuous-flow tests. The sorption rate of the metal uptake, together with the hydrodynamic parameters, determines the size of the contact equipment. These key process parameters could be used for comparison, for process design, and for scale-up purposes [257,273].

2.3.10. The future of biosorption

Biosorption application is facing great challenge, some investigators proposed several suggestion. The failure of the process commercialization is due to mainly nontechnical pitfalls involved in commercialization of technological innovations [258]. As solid capitalization is required for innovative process ventures, partnership approach is perhaps advisable. However, the choice of partners appears to be critical. For the future of biosorption, there are two trends of biosorption development for metal removal. One trend is to use hybrid technology for pollutants removal, especially using living cells [246]. Another trend is to develop good commercial biosorbents just like a kind of ion exchange resin, and to exploit the market with great endeavor [263]. The difficulties existing for biosorption application urge people to consider applying the hybrid technology which comprise of various processes to treat real effluents. Various biotechnology-based processes, such as biosorption, bioreduction and bioprecipitation were suggested. Consequently, application of living cells rather than dead cells for biosorption has gained attention again [158].

The above-mentioned bioprocesses along with other non-biotechnology based processes, for example, chemical precipitation, flotation, electrochemical processes, membrane technology, may also be helpful for treating wastewater in large-scale, even for simultaneous removal of organic substances and heavy metal ions in solution. Some examples have been reported [46, 207, 241]. All these processes may even possibly be realized in a single reactor; hence the corresponding novel reactors should be designed. The use growing microbes as a feasible alternative to pure biosorptive removal of metal contaminants from complex industrial effluents was advised [158, 246]. A hybrid technology either intra-biotechnological or inter-
technological, making use of a combination of various processes, including biosorption was suggested [246].

Biosorption is a desirable component in the design of flow sheets because the biosorption can effectively sequester dissolved metals out of dilute complex solutions in high efficiency and rapid intrinsic kinetics. These characteristics make biosorption an ideal candidate for the treatment of high volume low concentration complex waste waters [246]. Biosorption appears to be suitable as secondary or polishing applications for metal removal from dilute waste streams, which would be competitive with ion-exchange resin based on final cost-beneficial analysis, and the greatest use for biosorption may be in modular system for small companies, e.g. for specific treatment [83]. Another trend requires the improvement of biomaterials immobilization, as well as the optimization of the parameters of biosorption process and physicochemical conditions, including reuse and recycling. The mechanisms involved in biosorption or metal–microbe interactions should be further studied with great efforts [270].

Market factor for successful application of biosorption should be considered. From Volesky's viewpoint, the applications of certain types of biosorption are on the horizon, when the knowledge of biosorption is adequate, inviting the “new technology” enterprise ventures and presenting new and quite different challenges. The metals are only the “tip of the iceberg”. He pointed out a completely different type of biosorption, focusing on the purification and recovery of high-value proteins, steroids, pharmaceuticals and drugs like digoxin or vinblastin, not for environmentally oriented low-cost biosorption but for the product recovery of the high-priced pharmaceuticals. For example, antibodies as a biosorbent for locking and thus extracting, recovering and purifying the one desirable target molecule out of the mixture. [263, 273]

The sources and type of biosorbert play a major role in determining the overall cost of the biosorbent material. If the biomass needs to be specifically cultured for this purpose, manufacturers will incorporate maintenance and production expenses in the total cost, as well as a commercial fee. These costs can be minimal where certain biomass types such as photo-autotrophic
algae (e.g., Chlorella and Oscillatoria spp.) can be successfully grown for large-scale commercial use due to their minimal growth requirements (water, sunlight and CO$_2$). Marine algae such as S. fluitans and A. nodosum have shown biosorptive potential although the costs of harvesting the biomass may prove inhibitory to its application. Many industrial waste biomass types have been investigated for their biosorptive potential. These include the yeasts, S. cerevisiae from the food and beverage industry and Candida albicans, a clinical isolate; the moulds, R.arrhizus from the food industry, P. chrysogenum from antibiotic manufacturers and A. niger from citric acid and industrial enzyme producers; the bacteria, Bacillus spp., utilized in amino acid and antibiotic fermentations and Streptomyces noursei from the pharmaceutical industry. These potential biosorbents can usually be obtained relatively free of charge from the respective producers since they already present disposal problems to them. The only costs incurred should be those of drying, if required, and transport [273].

The researchers of various types of scientific background, from engineering to biochemistry, working together, will make a significant contribution to elucidating the biosorption mechanisms. Interdisciplinary efforts are mandatory and represent quite a challenge. The optimization of specific biosorption process applications has to be done in conjunction with industrial users/clients and requires specific process engineering expertise and a serious development capital commitment. A variety of investigation demonstrated that biosorption is a useful alternative to the conventional systems for the removal of heavy metal ions from aqueous solution. The development of biosorption process requires further investigation in the direction of modeling, of regeneration and immobilization of biosorbents, and of treating the real industrial wastewater [263].

2.3.11. Criteria for selection of a novel biosorbent

Routinely lots of biosorbents, such as bacteria, fungi and algae are discovered and distinguished by trial and experiments. Some easily available biomass in their native state or after simple processing have been tested for their biosorption performance, in particular the biowaste generated as a by-product of large-scale industrial fermentation, olive mill solid residues,
activated sludge from sewage treatment plants, biosolids, aquatic macrophytes, and other plant derived materials [8].

2.4. Application Feasibility and Consideration of the Biosorption Venture

The analysis of the feasibility of biosorption process was done in detail. They are optimistic on the biosorption future on a stage-wise approach. The assessment of the competing technologies (precipitation, reverse osmosis, ion exchange, bio-reduction), assessment of the market size, as well as assessment of cost of new biosorbents, all these should be considered with highest priority at the early stage in evaluation of the commercial potential and feasibility of application of the new technology based on the family of new biosorbent products [258]. After analysis, Volesky and coworkers proposed that huge markets already exist for cheap biosorbents, because a large amount of heavy metal is released into waters from various polluting industries, and also because ion exchange ion is expensive.

The partnership approach is advisable for demand of innovative process ventures, i.e., a solid capitalization. Identification of potential synergies and partners appears to critical considering biosorption as a direct competitor of ion exchange resin. A handful of huge transnational companies controlling the ion exchange resin market are difficult in operative decision making. Dynamic consulting companies are not capital-rich entities although in an excellent position to acquire and push new process technologies into the marketplace. Pioneering and propagation of innovative biosorption process is not appealing mining and ore processing companies although they appear to be excellent "clients" for innovative clean-up technologies. The above-mentioned aspects make the wide industrial application of biosorption difficult despite of its excellent performance from the R&D angle. [273]

Application of biosorption to treat the simulated AMD liquid waste, ready for demonstration tests, as an example, was introduced. From viewpoint of Volesky and coworkers, the enormous potential of biosorption application and its strong economic and technical advantages opens considerable market opportunities that can actually be quantified through a responsible market analysis [258]. Of course, there is still a lot of work required to do prior to the actual launching of the biosorption technology.
venture. Metal situation, the cost of biosorbents, the capacity and selectivity, the fate of exhausted biosorbent, all these should be considered. He compared biosorption with the several existing technology, including evaporation and reverse osmosis techniques, membrane processes, precipitation and classification techniques, activated carbon and ion exchange resin. Landfill or incineration still has their problems [256]. The feasibility of a potential biosorbent for inorganics removal from industrial effluents should be considered. The biosorption needs to effectively compete both on a cost and performance basis with existing methods before industry accept and implement it. These factors include:

The effluent characteristics, such as volume, type of contaminant and competitive ions, solution chemistry, pH and temperature adjustment; biomass characteristics, such as availability, mechanical stability, capacity, efficiency and metal selectivity of the biosorbent, ease of recovery and regenerative properties of the biomass, contaminant specificity and reaction kinetics, and immunity from interference by other effluent components or operating conditions; process characteristics, such as capital and operating costs, economic and performance equivalence to existing chemical and physical processes, batch/continuous and land space requirements. In fact, proper and cheap immobilization techniques are vital for biosorption application, determining the design and type of process to be employed (batch/continuous) [28]. Some important features required for the successful application of biosorption technology to real situations was offered [135]. strengthened and pointed out that the limited understanding of the metal biosorption mechanisms has hindered the application of biosorption. Selection of industrial effluents for pilot testing has remained largely intuitive. Therefore, exploring the mechanism of metal uptake by dead biomass was a real challenge for the field of biosorption.

Cost is a major factor for application of biosorbent systems. The cost of biosorbents and the economic assessment of biosorption process was discussed. Harvesting and drying are the major costs from marine algal biomass types. Usually the immobilization of biomass is simple and inexpensive, thus the source of raw biomass was the final cost of a
biosorbent. The regeneration, kinetics, biosorption performance and the like are all important factors for the cost of a biosorbent process.

For successful application on a large scale, any operation needs to be economically viable. The feasibility of a biosorption process depends on such factors as: biosorbent uptake performance, the source of the raw biomass, biomass granulation and treatment, the desorption and regeneration processes used, often, the source of the biosorbent has a major impact on the feasibility of the operation. Biosorbents (biomass) should always be obtained from the least-expensive source, such as from the effluent of a fermenter, seaweeds from nearby bodies of water, algae, etc. The spent biosorbents can be regenerated at very low cost using water, so the material can be reused many times. A brief outline of establishing an enterprise based on the biosorption technology is described. The feasibility of applying the biosorption process into wastewater purification would best be assessed based on a stage-wise approach. A considerable amount of research on biosorbent materials has developed a solid basis of knowledge and indicated their enormous potential. The highest priority at the early stage would be the preliminary and approximate assessment of the commercial potential and feasibility of application of the new technology based on the family of new biosorbent products. Correspondingly, the preliminary stage should consist of some basic studies [268].

2.4.1. Assessment of the competing technologies

The current costs and market share of the established conventional processes for metal removal/recovery from dilute solutions or wastewaters have to be summarized and assessed. Similarly for new unconventional and even new biosorbent-based processes which are approaching the stage of application in the field. For cases when metal removal from contaminated industrial effluents is considered, the following process alternatives can be considered for a more detail evaluation and feasibility assessment.

2.4.2. Assessment of the market size

While it is known that the environmentally-based market for metal removal/detoxification of metal-containing (industrial) effluents is enormous, the actual figures to support this generally prevailing perception would be
most convincing although not essential for launching the Company enterprise. The ion exchange market is as well established as this technology itself. The manufacture and supply of ion exchange hydrocarbon-derived polymer-based resins is concentrated in the hands of a very few transnational giant chemical companies. A quantitative review of the potential clientele for the biosorption metal-removal process needs to be carried out for different countries where applications of biosorption technology would be considered. Comparison of costs between the conventional and the new technology establish the feasibility of biosorbent applications and their competitiveness in the market place. As the application of biosorbent technology proves cheaper and more competitive it is anticipated that new applications, otherwise perhaps not feasible, will significantly increase the size of the current market and the scope of potential clients for biosorption technology [260].

2.4.3. Assessment of costs of new biosorbents

Approximate costs of different types of raw biomass need to be ascertained, as well as the costs of processing the biomass into applicable biosorbent materials maintaining their high sorption efficiency. This stage will require travel and fact finding efforts necessary to reliably establish the exact costs and conditions under which waste industrial biomass can be obtained from the large-size industrial operators. Similarly for the price of ocean-based biomass of selected marine algae which has to be collected from high seas or offshore areas. Estimation of the costs of preprocessing and drying the raw biomass to prevent its degradation will have to be carried out for selected representative types of biomass available in large quantities. Preliminary technical work needs to be carried out on the processing necessary for biomass formulation into a biosorbent product suitable for process uses. It is anticipated that different raw biomass materials (algae, fungi, bacteria) will require different and specific treatment for their optimal formulation into finished ready-to-use products. This part would entail specifically planned small-scale laboratory work and preliminary optimization of the procedures involved resulting in an efficient biosorbent material. Ideally, all these preliminary assessments should be carried out simultaneously as part of a better quantitative estimation of the venture feasibility. They could also be
carried out simultaneously with the technically oriented pilot-plant efforts [260].

The first major challenge faced by biosorption researchers was to select the most promising types of biomass from an extremely large pool of readily available and inexpensive biomaterials [135]. When choosing biomass, for large-scale industrial uses, the main factor to be taken into account is its availability and cheapness [253, 257, 262]. Considering these factors, native biomass can come from industrial wastes, which should be available free of charge; organisms easily obtainable in large amounts in nature; and organisms that can be grown quickly or specially cultivated or propagated for biosorption purposes [253, 257]. A broad range of biomass types have been tested for their biosorptive capacities under various conditions at this point in time, but there are no limits to exploration of new biomass types having low cost and high efficiency. Biosorbents primarily fall into the following categories: bacteria, fungi, algae, industrial wastes, agricultural wastes, natural residues, and other biomaterials. The biosorptive capacity of a certain type of biosorbent depends on its pretreatment methods, as well as, on experimental conditions like pH and temperature. After choosing a form of cheap and abundant biomass, the biosorbent capability for removing a target pollutant can be derived through simple chemical and/or physical method(s) [201].

Some biosorbents can bind and collect a wide range of heavy metals with no specific priority, whereas others are specific for certain types of metals. When choosing the biomass for metal biosorption experiments, its origin is a major factor to be considered. Biosorbents must be hard enough to withstand the application pressures, porous and/or “transparent” to metal ion sorbate species, and have high and fast sorption uptake even after repeated regeneration cycles. Biomass can come from:

- Organisms that can be obtained easily in large amounts in nature (e.g., bacteria, yeast, algae)
- Fast-growing organisms that are specifically cultivated or propagated for biosorption purposes (crab shells, seaweeds).
• Industrial wastes which should be obtained free of charge (Activated sludge, Fermentation waste)
• Other specially propagated biomasses.[268]

2.5. Bioreactors in biosorption

Using the biosorbents in functional bioreactor configurations, which complement metal uptake, could provide a system for lowering the heavy metal concentration in a solution. The media conditions and the physical environment in the bioreactor will affect the uptake achieved, therefore, changing and monitoring variables affecting the environment and media would provide researchers with the maximum heavy metal removal possible in any one configuration. A bioreactor is a system which may contain and support an organism during a desired process. The bioreactors have defined and controllable environmental factors and are therefore an efficient way of exploiting capabilities of biological systems [100]. They have proven to be useful in both research and industry since the internal environment is usually easily manipulated and monitored.

Factors affecting the efficiency of a process and a system therefore have to be defined and optimized. These may be temperature, nutrient availability, oxygen supply and demand, pH, mixing, agitation and mass transfer. There are numerous bioreactors with varying configurations to meet different requirements, which could be divided into two major groups – batch reactors and continuous reactors. Two main categories of bioreactors are used in bioremediation, suspended growth and fixed film bioreactors. Suspended growth bioreactors consist of batch, plug flow and completely mixed reactors. Microorganisms here are suspended in the medium in the reactor. Fixed-film bioreactors consist of fixed beds, fluidized beds, air-sparged, or rotating media reactors. Here, the microorganisms grow on or within a solid medium in the reactor.[100]

Individual reactors can be classified in four different ways [28]:

- Based on combination of the mode of substrate addition and the reactor geometry (i.e., continuous tubular packed bed).
- Based on the configuration of the biomass in the reactor (i.e., freely suspended or immobilized),
The method for providing the mixing within the reactor (i.e., mechanical agitation or gas agitation),

Based on the type of biocatalyst or enzyme used in the reactor (i.e., aerobic microorganisms or anaerobic microorganisms).

The application of biosorption in continuous processes has received increasing attention from researchers because of its potential industrial roles. Many different types of process configurations such as fixed bed upflow and downflow reactors, fluidised beds, rotating biological contactors, trickle filters and air-lift (either free or immobilised) reactors have been proposed and investigated for their practicality, [28]. Many different types of process configurations, such as stirred tank reactors, up-flow or downflow packed bed reactors, fluidized bed reactors, rotating contactors, trickle filters and air-lift reactors, have been proposed and investigated for their industrial practicality [28, 98, 158]. Most of these have been used in applications that employ living microorganisms for removal of metal contaminants from complex industrial wastewaters [58, 100].

Among the continuous biosorption reactors, the down-flow packed bed reactor should theoretically be the most cost effective system, due to its complete dependence upon gravitational forces to transfer the water body through the bed. All other systems require either pumps or motors with associated power consumption to effectively contact the waste water with the biosorbent. However, in downflow processes the operator has little control over effluent retention times within the reactor (retention time is governed by inter-particle spaces, bed volume/depth and biosorbent density). The waste stream may then be required to pass through numerous treatment cycles or reactors (in series) before desired metal concentrations are obtained. Another disadvantage of this system is the potential for compaction of the bed with consequential backflow of the waste stream due primarily to increased retention times. To alleviate this drop in pressure, the biosorbent should be loosely packed and immobilized in such a way that particles maintain their structural integrity for the duration of the reaction [28]. Stirred tank reactors may be operated in combination with a membrane system for liquid-solid separation. Fluidized bed reactors have low mass transfer limitation relative to
packed bed reactors. However, these reactors have been very rarely used for the purpose of biosorption using dead biomass. To achieve simple liquid-solid separation, some hybrid processes have been suggested in the literature. The ‘biosorptive flotation’ process was studied since 1993 [293, 292]. Most recently, a biosorption process using bio-functional magnetic beads has been proposed by a few researchers [146, 201].

The decision whether to use batch or continuous treatment is a function of hydraulic flow, types of contaminants present, space availability and invested capital. Usually, if flow rates are less than 20000 l shift⁻¹, manual batch treatment is most economical. Manual batch systems are simpler to operate as automated systems are prone to problems such as operator inattention to care and calibration of control instruments. If a manufacturing plant owner wishes to eventually expand his operation, installation of a continuous system from the outset may be the most cost-effective long-term answer [28].

Down flow column reactors should theoretically be the most cost-effective systems to operate due to their total dependance upon gravitational forces to transfer the water body through the bed. Consequently, the up-flow packed bed reactor, commonly called a column reactor, has been more extensively used in laboratory study, owing to its high operational yield and the relative ease of scaling up procedures to industrial capacities [256, 263]. In fact, column biosorption reactor is a simple and reproducible method, and is commonly used to assess the pollutant removal performances of a biosorbent operating in a continuous mode.

2.5.1. Fluidized Bed Column Sorption System

Biosorbent granules are fluidized in the column bed by upward flowing liquid. The main advantage of this arrangement is that the feed stream does not need to be completely particle free. The major disadvantage of the fluidized bed system is that it cannot utilize the biosorbent charge to its maximum potential because its contents are being mixed. This way the sorption driving force of the metal concentration gradient between the solid and liquid phases is always lower and it is more difficult to achieve a well polished effluent. Portions of used-up saturated biosorbent could be removed
from the column bottom while fresh biosorbent is added at the top. Clear treated effluent flows out the top where it is in contact with the relatively most fresh biosorbent. The fluidized bed is more expanded taking up 30-40% more volume. The fluid bed contactor typically consists of a 3.0 m high cylindrical column filled to slightly more than half with biosorbent which then expands upon fluidization. Even very high flows (200,000 Ld\(^{-1}\)) can be conveniently handled by such systems which can be modularly combined in parallel [260]. The advantages include: allows handling of (dilute) suspensions, gravity-separation of particles possible, sorption particle attrition and loss, pretreatment is necessary. The demerits associated were: Increased reactor volume, power requirement for fluidization, less effective and more complicated sorbent regeneration, no preliminary solid/liquid separation.

2.5.2. The Completely Mixed Sorption System

In this type of a contact system the concentration gradient, important for effective sorption, is much diminished. In a one-stage system the concentration of the sorbate throughout the mixed contactor is the same as in its effluent. This type of a sorption system may be useful in the following cases: the effluent concentration is not of concern (metal recovery); the biosorbent is in a powder or granular form; there needs to be a solid/liquid separation step (e.g. a screen or filtration of the sorbent); Several systems with intermittent solids concentration steps can be effectively operated in a counter-current series process arrangement [260].

The mixing in the sorption contactors is either mechanical or pneumatic. The sorption suspension has to be relatively dilute to allow mixing. Correspondingly, the volumes of contactor vessels are large. Mixed bed contactors are often utilized in series in order to handle the large volumes of inflow and to assure effluent standards. The number of stages and the residence time of the solution in each contactor is determined for the desired optimum performance of the system.

Different flow schemes of CSTRs (Continuous Stirred Tank Reactor) then may be utilized. Counter-current contact between the sorbate-laden liquid and the solid sorbent is more efficient. Fresh 'hungry' sorbent is fed where it meets the leanest liquid at the exit. Then the gradually more
saturated sorbent proceeds through the stages of the process contacting richer and richer liquid. The sorbent leaves the process at the point of the most sorbate-rich liquid inlet. That way the sorbent leaves saturated at the highest sorbate concentration. In order to achieve the counter-currency of the operation (Figure 10) there has to be a solid-liquid separation between the stages which separates the solid sorbent stream flowing in one direction from the liquid which flows in the opposite direction (e.g. granular activated carbon in the ‘carbon-in-pulp’ extraction of gold from ore suspensions). While this type of operation requires suitable granulation of the solid sorbent, it allows working with slurry (pulp) instead of clear liquid [260].

The performance of a serial counter-current operating sorption scheme actually approaches that of the fixed-bed column as the number of its stages approaches infinity. While the completely mixed CSTR is on one extreme of the scale, the theoretical plug-flow reactor (fixed-bed plug-flow column) represents the other extreme, theoretically with no mixing whatsoever. Fluidized bed reactors are partially mixed and on the theoretical scale would be placed somewhere between the CSTR and the plug-flow fixed-bed column.

2.5.3. Fixed-Bed Sorption System

Biosorbent granules are tightly packed, however, allowing the metal-bearing stream to freely pass through the column (usually downward). Dissolved metals are gradually removed from the liquid phase which always meets fresher and fresher sorbent as it trickles down the bed. Effluent leaving the column contains extremely low residual metals in the range of 10-50 ppb, often undetectable. When the biosorbent in the column eventually becomes fully loaded and the effluent metal concentration at the exit starts gradually increasing, the column is shut down and the flow is diverted into a second stand-by fresh column (the break-through point). Virtually unlimited scale-up of the process is accomplished by using batteries of multiple columns that work in parallel and/or in series to optimize the performance of the process [260].

The advantages include;
Most effective configuration, continuous-flow operation
virtually unlimited scale-up, no solid/liquid separation, in situ regeneration and washing.

The demerits associated were:
Cannot handle suspensions, requires column alternation, scales up by multiplying units, sensitive to pressure drop, complex valve and pipe systems.

2.5.4. Rotating Biological Reactor (RBC)

A fixed film of microorganisms is established on a contractor, which is constructed from sets of discs fixed to a central horizontal shaft. The shaft may be 3-7 m long and is supported on bearings in semicircular steel, glass reinforced plastic or concrete tank so that about 40% of the contactor lies below the surface of the effluent to be treated. The shaft is turned slowly and the attached biomass is alternately submerged in the effluent where it absorbs metals or raised out of the liquid so that the microorganisms absorb oxygen. The RBC provides an effective means of alternatively submerging a film of microorganisms in a substrate medium and then exposing the film to air for oxidation. A very large surface area is provided in a small volume of substrate, thereby permitting an excellent transfer of nutrients and oxygen necessary for bacterial metabolism. It offers several significant advantages such as low energy requirements; low space requirements, simplicity of operation; low maintenance requirements, high treatment efficiency and resistance to shock loads [100].

2.6. Status of Biosorbent Studies

Heavy metal interaction with anaerobically digested sludge was investigated using copper, cadmium and nickel chloride salt solutions. The behaviour of the well-known glycine-metal aqueous system was compared with the behaviour of the sludge-metal system. When equilibrium pH values are presented against the initial metal concentration for the glycine-copper system the profile obtained shows a sharp peak. This behaviour is similar to the behaviour of the experimental sludge copper system. The peak also appears for cadmium and nickel-glycine systems. However, it is not as pronounced as in the glycine-copper system and cannot be observed in the sludge-metal systems. The similar behaviour of both copper systems suggests that the metal binding mechanism of the sludge involves amino acid
functional groups which are present in the cell wall. Due to this similarity, an apparent molarity of the sludge can be evaluated by sludge titration with copper(II). The value obtained can be expressed as mmols of equivalent glycine per gram of sludge [27].

The uptake of phenol and nickel(II) ions, both singly and in combination, by dried aerobic activated sludge was studied in a batch system. The effects of initial pH and single and dual-component concentrations on the equilibrium uptakes were investigated. The optimum initial biosorption pH was determined as 4.5 for nickel(II) ions and as 1.0 for phenol. Multi-component biosorption studies were performed at these two initial pH values. It was observed that the equilibrium uptakes of phenol and nickel(II) ions were changed due to the initial biosorption pH and the presence of other components. Higher adsorption capacities for selective or simultaneous removal of phenol and nickel(II) could be carried out in a batch reactor by adjusting the pH of waste water and diluting waste water to the lower levels of phenol and nickel(II) concentrations. Since real wastewater will contain all kinds of pollutants, multi-component systems need further detailed study. It has been demonstrated previously that dried activated sludge offers interesting possibilities as a cation and an organics biosorbent, showing rapid binding [15].

The influence of pH, competitor ions (NaNO₃) and aerobic and anaerobic stabilization of activated sludge on the cadmium uptake by activated sludge solids was investigated. Above 0.08 mg l⁻¹ cadmium in solution, biosorption was found to follow the Freundlich isotherm. Active cellular uptake of soluble cadmium does not appear to be a significant mechanism of the biosorption. In addition, the cadmium uptake was not completely reversible. The adsorption of cadmium by activated sludge seems to involve a physico-chemical mechanism with especially weak electrostatic interactions with ion-exchange reaction. The optimum adsorption pH was 7.5. Adsorption is influenced by sodium ion concentrations up to an equivalent conductivity of 10000 µS cm⁻¹. The fact that the sludge stabilization level affected the sorption of cadmium might be explained either by a greater available adsorption surface per weight unit, or by alteration of the nature of
exoplymers and adsorption sites. Systematically aerobic and anaerobic stabilization of activated sludge increased the initial adsorption capacities. Respirometric measurements were done to evaluate the inhibitive effects of cadmium on activated sludge. Monod's equation and the equation of non-competitive inhibition were used to describe the toxicity related to cadmium uptake. These two equations appear to be complementary [32].

The equilibrium uptake of phenol and nickel(II) ions, both singly and in combination, by dried aerobic activated sludge was studied in a batch system. The optimum biosorption pH values were determined as 4.5 for nickel(II) and as 1.0 for phenol. Adsorption isotherms were developed for both the single- and dual-component systems at these two pH values and expressed by the mono- and multi-component Langmuir, Freundlich and Redlich–Peterson adsorption models and model parameters were estimated by the non-linear regression method. It was seen that the mono-component adsorption equilibrium data fitted very well to the Redlich–Peterson model for both the components and for both the pH values while all the multi-component adsorption models adequately predicted the multi-component adsorption equilibrium data at moderate ranges of concentration. In industry, effluents rarely contain a single component; hence sorption systems design must be based on multi-component effluents, making multi-component equilibrium data a necessity. The obtained data also showed that although dried activated sludge had a higher adsorption capacity at single component situation, the uptake from the binary mixture decreased in the presence of other component due to the initial pH and the levels of phenol and nickel(II) concentrations.

The model parameters obtained in this work can be used to estimate reactor volume, required biosorbent quantity for desired separation, purification degree, etc. from mass balance in a batch mono-component or binary system with satisfactory agreement with experimental results. Moreover, using these data multi-stage continuous systems can be also designed and stage number can be found for desired purification. The study indicated that the abundantly and cheaply available dried activated sludge can be used as an efficient biosorbent material for selective or simultaneous removal of single phenol, single nickel(II) and binary phenol–nickel(II)
mixtures from wastewaters and the biosorption equilibrium of these systems can be defined mathematically with proposed adsorption models. Although the mathematical models were developed for one and two component systems, the models may be applicable to other multi-component systems, which can represent real wastewater systems [14].

The sufficient removal of heavy metals from sewage sludge remains to be achieved. Heavy metals that exist in the sludge seem to be dissolved by acid treatments. This study shows that heavy metals in sewage sludge can be removed easily by treating a sludge filter cake with phosphoric acid containing hydrogen peroxide for 1.0° h at room temperature. Phosphoric acid of 8% concentration with hydrogen peroxide showed good removal rates of heavy metals comparable to those by 1°N hydrochloric acid. Copper is easily removed from the sludge in the presence of hydrogen peroxide. From the results of the investigation of the solubilities of several copper compounds into phosphoric acid with or without hydrogen peroxide, the copper in the sludge does not exist as copper sulfides, but it seems to exist as copper thiolates containing Cu(II) in biopolymers. In this process, the phosphoric acid used for the removal of heavy metals is almost entirely recovered and is reused. Sewage sludge with low content of heavy metals can be recycled as a useful resource [226].

The ability of dried anaerobic activated sludge to adsorb phenol and chromium(VI) ions, both singly and in combination was investigated in a batch system. The optimum initial biosorption pH for both chromium(VI) ions and phenol was determined as 1.0. Multi-component biosorption studies were also performed at this initial pH value. It was observed that the equilibrium uptakes of phenol and chromium(VI) ions were changed due to the presence of other component. Adsorption isotherms were expressed by the mono and multi-component Langmuir, Freundlich and Redlich–Peterson adsorption models and model parameters were estimated by the non-linear regression. It was seen that the mono-component adsorption equilibrium data fitted very well to the non-competitive Freundlich and Redlich–Peterson models for both the components while the modified Freundlich model adequately predicted the
multi-component adsorption equilibrium data at moderate ranges of concentration.

Although dried anaerobic activated sludge had a higher adsorption capacity for phenol and chromium(VI) at single component situation, the adsorption uptake of phenol and chromium(VI) in the binary mixture were found to be decreasing due to the levels of phenol and chromium(VI) concentrations because of the antagonistic interaction between the components. Industrial effluents rarely contain a single component, hence, adsorption systems design must be based on multicomponent systems. It could be said that phenol–chromium(VI) multi-component system could be defined with all the proposed competitive adsorption models. In mixtures of two or more components in a solution, the synergistic or antagonistic interaction occurring between the components may affect the individual component uptake by the microorganism.

The most logical reason for this behaviour was claimed to be the competition for similar binding sites on the surface of cells and/or the screening effect by the second component. It was concluded that all the adsorption models agreed well with the results found experimentally in the studied concentration ranges except at very high total initial concentrations of both components. It has been demonstrated previously that dried activated sludge offers interesting possibilities as a metal ion and an organic biosorbent, showing rapid binding [17].

The biosorption of chromium(VI) and nickel(II) ions, both singly and in combination, by dried activated sludge was investigated in a batch system as a function of initial pH and single- and dual-metal ion concentrations. The working initial pH values for single chromium(VI) and nickel(II) biosorptions were determined as 1.0 and 4.5, respectively. It was observed that the co-ion effect on the equilibrium uptake became more pronounced as the co-ion concentration in solution increased and pH level increased for chromium(VI) and decreased for nickel(II). Adsorption isotherms were developed for both the single- and dual-metal ion systems at these two pH values and expressed by the mono- and multi-component Langmuir and Freundlich adsorption models and model parameters were estimated by the non-linear regression. It
was seen that the mono-component adsorption equilibrium data fitted very well to both the monocomponent adsorption models for both the components and the pH values studied while the multi-component Freundlich adsorption model adequately predicted the multi-component adsorption equilibrium data at moderate ranges of initial mixture concentrations for both the studied pH values.

It was concluded that multicomponent Freundlich model agreed well with the results found experimentally in the studied initial mixture concentration range at both the studied pH values. This work could enable to extrapolate the prediction of adsorption equilibria of the binary system if experimental data are not available for a certain level of bisolute concentrations. Since real wastewaters will contain all kinds of pollutants, adsorption systems design must be based on multi-component effluents, making multicomponent equilibrium data a necessity. Although dried activated sludge had a higher adsorption capacity for chromium(VI) and nickel(II) at single-component situation due to the initial pH of solution, the equilibrium uptake of chromium(VI) and nickel(II) in the binary mixture were found to be decreasing due to the levels of chromium(VI) and nickel(II) concentrations because of the antagonistic interaction between the components [12].

Biosorption of Pb(II) and Cu(II) ions in single component and binary systems was studied using activated sludge in batch and continuous-flow stirred reactors. In biosorption experiments, the activated sludge in three different phases of the growth period was used: growing cells; resting cells; dead or dried cells. Because of the low adsorption capacity of the non-viable activated sludge, especially in the case of Pb(II) ions, biosorption of the Cu(II) and Pb(II) ions from the binary mixtures was carried out by using the resting cells. The Freundlich model described the experimental equilibrium uptake of Pb(II) and Cu(II) ions by the resting activated sludge better than the Langmuir model. The results of the competitive biosorption studies showed that the Cu(II) [or Pb(II)] interfered with the uptake of Pb(II) [or Cu(II)]. The amounts of Cu(II) and Pb(II) ions adsorbed during the continuous metal- flow reported in this study were lower than the amounts adsorbed during the batchwise operation. Using a mathematical model based on continuous system mass
balance for the liquid phase and batch system mass balance for the solid phase, the forward rate constants for biosorption of Pb(II) and Cu(II) ions were 0.793 and 0.242 (mmol min$^{-1}$), respectively. The following conclusions were be drawn from the study; The resting cells were preferred to simulate the competitive biosorption behavior of Pb(II) and Cu(II) ions in batch and continuous-flow stirred reactor systems. The resting aerobic activated sludge can be used successfully as a biosorbent for the adsorption of heavy metals [213].

Aerobic granules have excellent settle ability and high-porosity structure. This study investigated the feasibility of aerobic granules as a novel type of biosorbent, for cadmium removal from industrial wastewater. Batch tests were carried out at different initial Cd$^{2+}$ and granule concentrations. Based on experimental data, a kinetic model was developed to describe Cd$^{2+}$ biosorption by aerobic granules. Results showed that the Cd$^{2+}$ biosorption on aerobic granule surface was closely related to both initial Cd$^{2+}$ and granule concentrations. The maximum biosorption capacity of Cd$^{2+}$ by aerobic granules was 566 mgg$^{-1}$. This study for the first time shows that aerobic granules have a high biosorption capacity to Cd$^{2+}$ and can be used as an effective biosorbent for the removal of cadmium or other types of heavy metals from industrial wastewater [152].

The biosorption of chromium(VI) and nickel(II) ions, both singly and in combination, by dried activated sludge was investigated in a batch system as a function of initial pH and single and dual-metal ion concentrations. The working pH value for single chromium(VI) and nickel(II) biosorption was determined as 1.0 and 4.5, respectively, due to the selective uptake of biomass. Multi component biosorption studies were performed at these two initial pH values. It was observed that the biosorption kinetics and equilibrium uptakes of chromium(VI) and nickel(II) ions in binary mixtures changed due to the initial biosorption pH and the presence of the other component. Since real wastewaters will contain all kinds of pollutants, adsorption system design must be based on multicomponent effluents, making its equilibrium data a necessity. Although dried activated sludge had a higher adsorption capacity for chromium(VI) and nickel(II) at the single-component situation due to the
initial pH of the solution, the equilibrium uptake of chromium(VI) and nickel(II) in the binary mixture was found to decrease due to the levels of chromium(VI) and nickel(II) concentrations because of the antagonistic interaction between the components. Although the order of second component addition affected the adsorption rate and uptake negatively, dried activated sludge offered a practical approach to the binary removal of chromium(VI) and nickel(II) from wastewater due to the pH of wastewater and the levels of metal ion concentrations [3].

The biosorption of copper ions from aqueous solution by dried activated sludge was investigated in batch systems. Effect of solution pH, initial metal concentration and particle size range were determined. The suitable pH and temperature for studied conditions were determined as 4.0 and 20°C, respectively. The theoretical maximum biosorption capacity of activated sludge was 294 mg g⁻¹ at 20°C for <0.063 mm particle size. The equilibrium data fitted very well to both Langmuir and Freundlich isotherm models. The pseudo-first and second-order kinetic models were used to describe the kinetic data. The experimental data fitted to second-order kinetic model. An increase in the initial metal concentration increases of biosorption capacity, which also increases with decreasing particle size. Dried activated sludge has different functional groups according to the FT-IR results. This study demonstrated that the activated sludge biomass could be used as an effective biosorbent for the treatment of wastewater containing Cu(II) ions. However activated sludge biomass is low cost natural abundant biomass and it may be alternative to more costly materials such as activated carbon [108].

The objective of the study was to explore the sorption mechanism of WPWS for heavy metals using nickel (Ni) as the sorbate. The WPWS has been characterized with wet chemistry, infrared (IR), X-ray diffraction, scanning electron microscopy (SEM), carbon- 13 magic-angle nuclear magnetic resonance (13C NMR), and energy-dispersive spectrometry chemical analyses. The sludge contained high organic carbon (40.5%), nitrogen (23.4%), and cation-exchange capacity (1218 cmolc kg⁻¹). SEM investigation of WPWS showed porous-like activated carbon. IR analysis of WPWS revealed that R-NH2 and R-COOH were the major functional groups.
The proportion of organic functional groups in WPWS quantified by 13C NMR analysis was in the following order: alkyl-C > carboxyl-C > N-alkyl-C > aromatic-C > O-alkyl-C> acetal-C > phenolic-C. The parameters affecting the sorption of Ni were the pH, initial concentration of Ni, particle size of WPWS, and reaction temperature. The sorption isotherms of Ni were only well described by the Langmuir sorption isotherm and the maximum sorption capacity is 66.55 mol g\(^{-1}\) at 50°C.

In the sorption kinetics, only the pseudo-second-order sorption equation fits the experimental results well. A higher initial concentration of Ni results in a decrease in the sorption rate of external diffusion. Under the steady-state reaction conditions, the Gibb free energy (\(\Delta G^0\)) ranges from -18.969 to -23.616 kJ mol\(^{-1}\), and \(\Delta H^0\) and \(\Delta S^0\) are 3.366 kJ mol\(^{-1}\) and 6.056 J mol\(^{-1}\)K\(^{-1}\), respectively, indicating that higher temperature favors spontaneous reaction. According to the thermodynamic sorption parameters under steady-state conditions, this sorption is a spontaneous and endothermic reaction. The sorption mechanisms include physical adsorption and chemical complexation. Amino and carboxyl groups are the prominent functional groups interacting with Ni. The WPWS, is an effective biosorbent of Ni in solutions because of its characteristics of rough surface texture, high CEC, high organic matter contents, and abundant amino and carboxyl functional groups [15].

Powdered waste sludge (PWS) was used for removal of copper(II) ions from aqueous solution by biosorption. Waste activated sludge obtained from a paint industry wastewater treatment plant was pre-treated with 1% hydrogen peroxide solution dried, ground and sieved to a number of fractions with different particle sizes. Biosorption capacity of pre-treated PWS for Cu(II) ion removal was investigated as function of particle sizes (external surface area), copper(II) and PWS concentrations and also pH using batch biosorption experiments. Biosorbed copper ion concentrations increased with increasing specific external surface area of PWS, initial Cu\(^{2+}\) concentration and pH, but decreased with increasing PWS concentration. Percent copper removal from the solution also increased with increasing external surface area or decreasing particle size of the adsorbent, PWS concentration and pH, but decreased with increasing initial copper ion concentration. The maximum
biosorption capacity was 156 mg Cu$^{2+}$ g PWS$^{-1}$ when PWS concentration was 0.25 g l$^{-1}$ with an average particle size of 64 mm. The initial volumetric rate of biosorption also increased with increasing specific external surface area of PWS resulting in nearly 70 mg Cu l$^{-1}$ h$^{-1}$ at a specific external surface area of 943 cm$^2$g$^{-1}$ with the smallest particle size (53 mm) tested. Optimal pH resulting in maximum biosorption was 5.0 with a minimum zeta potential (15.6 mV) on the surface of the PWS particles [195].

Waste sludge samples obtained from a paint industry wastewater treatment plant was dried, ground and pre-treated with 1% H$_2$O$_2$ to improve the biosorption capacity. The powdered waste sludge (PWS) was sieved to different mesh sizes with particle size of 64 nm and used for biosorption of zinc(II) ions from aqueous solution. The pseudo-first and second-order rate expressions were used to correlate the experimental data. The kinetic constants were determined for both models and the second-order rate expression was found to be more suitable. Three different biosorption isotherms were used to correlate the equilibrium biosorption data and the isotherm constants were determined. Those were the Langmuir, the Freundlich and the generalized biosorption isotherms. The Langmuir isotherm was found to fit the experimental data better than the other isotherms tested. Maximum biosorption capacity was found to be 82 mg Zn g PAS$^{-1}$. High biosorption capacity and low saturation constant of pre-treated PWS makes the adsorbent more attractive as compared to other alternatives. The paint industry waste sludge used for zinc ion biosorption was found to be superior to the waste sludges used by other investigators yielding higher biosorption capacity ($q_m$) and lower saturation constant (K) for the Langmuir isotherm [124].

Simultaneous biosorption of phenol and chromium(VI) ions to Mowital B30H resin immobilized activated sludge from binary mixture was studied and compared with single phase biosorption in a continuous packed bed column. The phenol and chromium(VI) binding capacity of biosorbent was shown as a function of single and dual pollutant concentrations at a flow rate of 0.8 ml min$^{-1}$ and at a pH value of 1.0. The equilibrium uptake (or column biosorption capacity) of each pollutant was determined by evaluating the breakthrough
curves obtained at different inlet concentrations changing 50–500 mg l\(^{-1}\) at 25\(^\circ\)C in single and binary systems. The maximum column biosorption capacity of dried activated sludge was 9.0 mg g\(^{-1}\) for phenol and 18.5 mg g\(^{-1}\) for chromium(VI) at single ion situation. The column sorption capacity of immobilized dried activated sludge for phenol [or for chromium(VI)] decreased notably due to the presence of other component. The mono and multi-component sorptions in packed bed were expressed by the Yoon and Nelson model to determine the kinetic constants and to predict the breakthrough curves of each component. The model constants belonging to the model were determined by linear techniques and were proposed for the use in column design.

Using the method of response surface analysis, the relation between Yoon and Nelson model rate constant of each component and the concentrations of each component in the binary sorption system was determined. Such relationships can be used to find rate constants in a mixture containing unstudied concentrations of phenol and chromium(VI). It seems that although the immobilization process decreased the biosorption properties of the biomass for each component, dried activated sludge may find promising applications for simultaneous removal and separation of phenol and chromium(VI) from aqueous effluents in a continuously operated packed column over a wide range of phenol and chromium(VI) concentration. The results also indicated that the sorption process could only deal with lower concentration of components if a high percentage removal was required for extended periods [11].

Batch equilibrium sorption experiments were used for screening for cost-effective four types of sludge, which were DWS (drinking water treatment plant sludge), LLS (landfill leachate sludge), ADSS (anaerobically digested sewage sludge), and SS (sewage sludge). SS removed cadmium most efficiently from aqueous solution (0.38 mmol/g), and showed the highest desorption efficiency (26.3%). Only the SS can be fitted by Langmuir isotherm model (\(r^2 = 0.996\)). The FT-IR spectra of SS and cadmium loaded SS indicated that carboxyl groups were major binding sites of cadmium binding sites. In kinetic experiment, it was found that the uptake of the metal
by the SS was accompanied with proton release, indicating that the metal binding occurs via an ion exchange as well as by electrostatic interaction between carboxylate groups and cadmium ions. This sorbent may have a potential for use as high-value biosorbent of heavy metals and it deserves further investigations into the details of practical application, for example on the development of desorption methods and on sorption process optimization [64].

The removal of Cd(II) and Pb(II) from aqueous solutions by using dried activated sludge has been investigated in batch systems. Effect of solution pH, initial metal ion concentration and temperature were determined. For the metal ions investigated the optimum adsorption was achieved at pH 6.0 and 4.0 for Cd(II) and Pb(II) ions, respectively. The results of the kinetic studies showed that the uptake processes of the two metal ions [Cd(II) and Pb(II)] followed the pseudo-second-order rate expression. The equilibrium data fitted very well to both the Langmuir and Freundlich adsorption models. The FT-IR analysis showed that the main mechanism of Cd(II) and Pb(II) biosorption onto dried activated sludge was their binding with amide I group. This study demonstrated that the use of readily available waste activated sludge biomass offers an alternative in the removal of metals from wastewaters [271].

Biosorption experiments were performed using different pretreated activated sludge as bioadsorbent for Cu^{2+}, Cd^{2+} and Ni^{2+}. Pretreatment with NaOH was found to improve the adsorption capacity of the sludge where as treatment with HCl reduces it. The treated and untreated sludge show great affinity towards Cu^{2+}, Cd^{2+} and low affinity towards Ni^{2+}. The maximum loading capacity of the NaOH treated sludge was 131.6 and 93.4 mgg\(^{-1}\) for Cu^{2+} and Cd^{2+}, respectively. It was found that both Langmuir and Freundlich isotherm models fit the adsorption data with the different types of sludge and ions. The value of \(r^2\) exceeds 0.95 in most cases. It was found that the maximum adsorption capacity drops 18.3% as the temperature increases from 25°C to 45°C. The adsorption capacity was found to increase as the adsorbent mass and mixing speed increase. It was found that there is an optimum value of the pH equal to 5 at which the adsorption capacity for the three sludge types was 97.5, 81 and 60 mgg\(^{-1}\). Desorption experiments
indicate that the desorption efficiency with 0.1 M H$_2$SO$_4$ solution reaches 94% in the first cycle and decreases to 8% in the 4th cycle after collecting 20,700 mg/l of Cd$^{2+}$ H$_2$SO$_4$. Based on experimental results the following conclusions can be drawn. Activated sludge can be easily applied as a cheap bioadsorbent for heavy metal ions such as Cd$^{2+}$, Cu$^{2+}$ and Ni$^{2+}$. The results obtained indicate that it is possible to design a continuous process for wastewater treatment by bioadsorbing the ions, followed by sludge regeneration and metal ions recovery [20].

Removal of Pb(II) by using anaerobically digested sludge (ADS) obtained from a nearby wastewater treatment plant was examined. Firstly, sorption kinetic and equilibrium experiments were conducted using agitated, thermostated (25°C) batch reactors. The maximum Pb(II) sorption capacity was found to be very high (1750 mg/g dry ADS or 8.45 mmol/g dry ADS) corresponding to over 99% removal efficiency at the initial Pb(II) concentrations below 1000 mg/l. At all initial Pb(II) concentrations tested, sorption resulted in neutralization with an increase in the solution pH from an initial value of 4.0–5.5 to an equilibrium value of 7.0–8.0, at which Pb(II) can precipitate as hydroxide, indicating effective neutralization, which makes the use of ADS more favorable in the treatment of acidic heavy metal bearing wastewaters. The removal of Pb(II) by ADS was found to involve bioprecipitation as well as biosorption. FTIR spectrometry highlighted carboxyl groups present on the surface of ADS as the major functional groups responsible for biosorption. Secondly, a three-stage semi-continuous pseudo-counter current reactor system was tested to reduce ADS requirement in comparison to a conventional single-stage batch reactor. At an initial Pb(II) concentration of about 200 mg/l, an effluent Pb(II) concentration of 1.3 mg/l was achieved in the three stage reactor, corresponding to a metal removal capacity of 682.7 mg/g dry ADS (3.30 mmol/g), in comparison to 1.9 mg/l and 644.0 mg/g dry ADS (3.10 mmol/g) for the single-stage batch reactor. In the present study, Pb(II) removal by ADS has been investigated. ADS was found to be very effective in the removal of Pb(II) with a maximum removal capacity of about 1760 mg (8.5 mmol) Pb(II) per gram of biomass Multiple
stage reactor configuration appeared to be more effective than single stage [242].

This study investigated the feasibility of anaerobic granules as a novel type of biosorbent, for lead, copper, cadmium, and nickel removal from aqueous solutions. Anaerobic sludge supplied from a wastewater treatment plant in the province of Quebec was used. Different ionic forms of anaerobic biomass were evaluated in terms of metal binding capacity. The Ca-biomass was found to have the highest uptake capacity. After treatment of the biomass with Ca ions, the cation exchange capacity of the biomass was approximately 111 meq100g^-1 of biomass dry weight, which is comparable to the metal binding capacities of commercial ion exchange resins. This work investigated the equilibrium, batch dynamics for the biosorption process. Binding capacity experiments using viable biomass revealed a higher value than those for nonviable biomass, while using non-viable biomass treated with Ca revealed a high value of metals uptake. The solution initial pH value affected metal sorption. Over the pH range of 4.0–5.5, pH-related effects were not significant. Meanwhile, at lower pH values the uptake capacity decreased.

The uptake of metals was very fast. Within the first 5 min of contact, nearly 75% of the total metal uptake was completed. Time dependency experiments for the metal ions uptake showed that adsorption equilibrium was reached almost 30 min after metal addition. It was found that the q_{max} for Pb^{2+}, Cd^{2+}, Cu^{2+}, and Ni^{2+} ions, were 255, 60, 55, and 26 mgg^-1 respectively. The data pertaining to the sorption dependence upon metal ion concentration fitted to Langmiur isotherm model. Based on the results, the use of non-living anaerobic biomass as biosorbent promising biosorbent for removal of heavy metals from wastewater due to its optimal uptake of heavy metals, its particulate shape, compact porous structure, excellent settling ability, and its high mechanical strength, the solution pH affected metal sorption.

The Ni^{2+} biosorption by aerobic granular sludge was studied at various initial pH values. Results showed that the initial pH would play an important role in the Ni^{2+} removal by aerobic granules and affected the zeta potential of aerobic granules. A thermodynamic equilibrium isotherm previously developed fitted the experimental data very well at all studied pH values. It
was demonstrated that the electrostatic attraction mechanism could provide a good explanation for the relationship between the zeta potential of aerobic granules and Ni$^{2+}$ biosorption, while the large quantity of K$^+$, Mg$^{2+}$ and Ca$^{2+}$ released during the Ni$^{2+}$ biosorption indicated that as the ion-exchange mechanism was involved in the Ni$^{2+}$ biosorption by aerobic granules. It was also found that some light metals, such as K$^+$, Mg$^{2+}$ and Ca$^{2+}$ would be released into the bulk solution during the Ni$^{2+}$ uptake onto the aerobic granules, which in turn indicated that ion-exchange was one of the Ni$^{2+}$ biosorption mechanisms. Ni$^{2+}$ biosorption by aerobic granules and the zeta potential of aerobic granules were pH dependant. The Ni$^{2+}$ biosorption capacity increased with the increase of pH in the range of 2–6 and attained a maximum value at pH 6. The model proposed previously could predict the nickel biosorption at various initial pH values very well [150].

Biosorption of heavy metal ions, such as Cu$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$, was carried out using waste activated sludge and municipal sewage treatment plant as adsorption material. The effects of parameters, such as pH value, temperature, reaction time and sorption duration, were studied. The results indicated that the removal rates of Cu$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ with low concentration were 96.47%, 80% and 90%, respectively, sorbed by waste activated sludge. Little effect of dosage of activated sludge on the adsorption of Cu$^{2+}$ and more effects on the adsorption of Zn$^{2+}$ and Cd$^{2+}$ are observed. Little effect of temperature is observed, while pH value and adsorption time exert important influence on the sorption process. The adsorption behaviours of heavy metal ions all have parabolic relationships with pH value. The optimum pH value was between 6 and 10, and the optimum adsorption time was 1 hr. In single heavy metal ion system, the sorption processes of metal ions were in accordance with Freundlich model. The Freundlich model fits better for Cu$^{2+}$, Cd$^{2+}$ than Langmuir model, the model for Zn$^{2+}$ is on the contrast, which indicates that it is suitable for the treatment of these three heavy metal ions using intermittent operation. In addition, the sorption capacity of the sludge for Cu$^{2+}$ is preferential to the other two ions.

Powdered waste sludge (PWS) obtained from a paint industry wastewater treatment plant and pretreated with 1% H$_2$O$_2$ was used for
biosorption of Zn(II) ions from aqueous solution. The effects of operating conditions, pH, temperature, agitation speed, PWS particle size, Zn ion and PWS concentrations on the extent of Zn ion biosorption were investigated in batch experiments. The extent of Zn biosorption increased with increasing pH due to the negative charges on PWS surfaces at high pH levels. The optimum pH resulting in maximum Zn ion biosorption was found to be pH = 5, since Zn ions precipitated in the form of Zn(OH)₂ at pH levels above 5.0. The rate and extent of Zn ion biosorption increased with temperature between 25°C and 50°C due to the higher frequency of interactions between adsorbent and sorbate at elevated temperatures. However, the rate and extent of biosorption were not particularly sensitive to temperature variations since the activation energy was low at 4.5 Kcalmol⁻¹. Biosorbent particle size had a significant effect on Zn ion biosorption, yielding high percentage Zn removals at small particle sizes (Dₚ < 100 μm) or large surface areas of PWS. Rotational speed affected the transfer rates of Zn(II) ions onto the adsorbent surfaces by affecting the hydrodynamical conditions and therefore, the rate and extent of Zn ion removal by biosorption. Rotational speed should be above 150 rpm in order to overcome mass transfer limitations and to obtain high percentage Zn ion removal. Initial Zn ion and PWS concentrations affected the extent of Zn ion biosorption significantly since biosorption is based on interactions between the adsorbent and the adsorbate like a bimolecular reaction. At constant biosorbent (PWS) concentration, percentage Zn ion removal decreased, but the biosorbed Zn concentration increased with increasing initial Zn ion concentration. However, at constant initial Zn concentration, percentage Zn removal increased, but the biosorbed Zn ion concentration decreased with increasing PWS concentration. At low PWS concentrations the extent of biosorption was limited by the available surface area or the number of binding sites of the PWS. However, the limiting factor was Zn ion concentration at high PWS concentrations. The maximum biosorption capacity of PWS for Zn ions was found to be 168 mgg⁻¹ with 0.25 gl⁻¹ PWS and 200mgl⁻¹ Zn ion concentration (Dₚ = 64 μm). The optimum pH resulting in maximum Zn ion biosorption was found to be pH 5 since Zn ions precipitated in the form of Zn(OH)₂ at pH levels above 5.0. The rate and extent of Zn ion biosorption...
increased with temperature between 30 °C and 50 °C. This value is superior to those reported in the literature, indicating that PWS is an effective biosorbent for Zn ion removal from aqueous solutions [124].

The present study was carried out for evaluating the retention behaviour of sanitary sewage and sand in relation to chromium and nickel ions in upflow reactors. It was found that the sludge presented a greater assimilation of the metals studied when compared to the inert material, probably due to the presence of anionic groups, which favours adsorption and complexation processes. Thermal analyses of the samples showed a shift in the decomposition peaks of the "in natura" sludge, when compared with those of the samples spiked with the metals, confirming the possibility of interactions between the heavy metals and the anionic groups present in the sludge. Results of the biosorption of Ni(II) and Cr(III) by the utilization of WS in upflow reactors demonstrated an efficient removal of the metals. Higher biosorption capacity values at pH higher than 7.0 were observed. This increase in pH may be due to the hydrolytic protonation of the biomass due to the action of the metallic solution on the biosorbent. Biosorption of the metallic ions occurred more intensely in the columns loaded with wastewater sludge in comparison to the columns with inert material, which was ascribed to the more effective complexation action due to presence of chemisorption and physisorption phenomena promoted by the organic and inorganic compounds existing in this type of biosolid. The DSC and TG studies of the samples demonstrated that the shift of the final thermal decomposition peaks of the samples WSNi and WSCr in relation to the sample WS evidenced the existence of an interaction of physicochemical nature between the metals and the sewage sludge. This fact was also confirmed by the energy sorption evidenced by the endothermic behaviour of the samples. The increase in ash contents that represent inorganic fraction in WSNi and WSCr samples in relation to the sludge sample indicated the presence of the metals after the biosorption process [31].

The biosorption of different metals (Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+} and Pb^{2+}) was investigated using activated sludge. The optimum pH was 4.0 for Cd, Cu and Pb sorption and 5.0 for Ni and Zn. Biomass metal uptake clearly
competed with protons present in the aqueous medium, making pH an important variable in the process. Protons consumed by biomass in control tests versus protons exchange in biosorption tests confirmed a maximum exchange between metal cations and protons at pH 2.0. The study of the influence of biomass concentration revealed that the amount of protons released from biomass increased with biomass concentration. This would confirm the hypothesis of ion exchange between both types of ions. The data pertaining to the sorption dependence upon metal ion concentration fitted the Langmuir isotherm better than the Freundlinch model. The maximum sorption uptake of the studied metals by the activated sludge showed the following decreasing order: Pb< Cu< Cd< Zn< Ni. Desorption experiments showed that HCl was a good eluent for the five metals tested, particularly at low pH values (1 and 2). At pH 3 or 4 the desorption yield was significantly lower. However, its use did not allow the reuse of biomass in subsequent loading and unloading cycles. EDTA was also a good desorption agent, achieving the total recovery for the five metals tested at a concentration of 1mM, with the advantage that biomass could be reused for three sorption–desorption cycles [109].

Effects of operating parameters such as pH, temperature, adsorbent concentrations and particle size on batch biosorption kinetics of copper(II) ions onto pre-treated powdered waste sludge (PWS) were investigated. Pseudo-first and second order kinetics was used for correlation of pre-equilibrium biosorption data and the rate constants were determined. The pseudo-second order kinetics was found to be more suitable for representation of the kinetic data for almost all cases. Kinetic constants increased with increasing pH, temperature and PWS concentration, but decreased with increasing Cu(II) concentrations and the particle size of PWS. The rate constants of both models increased with increasing pH from 3 to 6 due to increasing negative surface charges of PWS and also less competition with the Cu(II) ions by the lower H+ concentrations in solution. The highest rate constants for the pseudo-first and second order kinetics were 0.808 h\(^{-1}\) and 0.0309 mgg\(^{-1}\) h\(^{-1}\), respectively for the smallest particle size of 53 nm. The highest Cu(II) biosorption capacity of 156 mg g\(^{-1}\) was obtained with PWS and
Cu(ll) concentrations of 0.25 g l\(^{-1}\) and 100 mg l\(^{-1}\) with the smallest particle size \(D_p<53\text{nm}\). The rate constants for both models increased with decreasing particle size due to larger total surface area of particles at small particle sizes. Biosorption should be carried out at low particle sizes of the adsorbent. The biosorption should be carried out at pH 5 to obtain high rates. The rate constants increased with increasing temperature due to higher energy levels and frequency of interactions among the adsorbate and the adsorbent species at high temperatures. The activation energy according to the second order kinetic model was 11.69 kcal mol\(^{-1}\) indicating high degree of sensitivity of the biosorption rate to temperature changes. Cu(ll) concentrations below 100 mg l\(^{-1}\) were preferred for high rates of biosorption. High PWS concentrations were preferred for high rates of biosorption. However, due to adsorbent particle agglomeration adsorbent concentrations above 3.0 g l\(^{-1}\) are not recommended [196].

Biosorption of zinc(ll) ions onto pre-treated powdered waste sludge (PWS) was investigated using a completely mixed tank operating in fed-batch mode instead of an adsorption column. Experiments with variable feed flow rate (0.05–0.5 l h\(^{-1}\)), feed Zn(ll) ion concentrations (37.5–275 mg l\(^{-1}\)) and amount of adsorbent (1–6 g PWS) were performed using fed-batch operation at pH 5 and room temperature (20–25\(^{\circ}\) C). Break-through curves describing variations of aqueous (effluent) zinc ion concentrations with time were determined for different operating conditions. Percent zinc removal from the aqueous phase decreased, but the biosorbed (solid phase) zinc ion concentration increased with increasing feed flow rate and zinc concentration. A modified Bohart–Adams equation was used to determine the biosorption capacity of PWS \((q_{\text{ds}})\) and the rate constant \((K)\) for zinc ion biosorption. Biosorption capacity \((q_{\text{ds}} = 57.7 \text{ g Zn kg}^{-1} \text{ PWS})\) of PWS in fed-batch operation was found to be comparable with powdered activated carbon (PAC) in column operations. However, the adsorption rate constant \((K = 9.17\text{m}^3 \text{ kg}^{-1} \text{ h}^{-1})\) in fed–batch operation was an order of magnitude larger than those obtained in adsorption columns because of elimination of mass transfer limitations encountered in the column operations. Therefore, a completely mixed tank operated in fed–batch mode was proven to be more advantageous
as compared to adsorption columns due to better contact between the phases yielding faster adsorption rates [123].

This study investigated the biosorption kinetics and equilibrium of cadmium, nickel and zinc by activated sludge from a biological nutrient removal (BNR) process. A series of batch experiments with different initial metal concentrations were conducted to determine the metal removal from BNR sludge. The harvested sludges were from a continuous-flow anaerobic anoxicoxic (A2O) system, operated under a 10 days of sludge retention time. Batch tests were specially designed to isolate the precipitation effects of metal ions in solution so as to compare the isotherm constants of biosorption with and without precipitation isolation. Experimental results revealed that BNR sludge exhibited two stages of biosorption, i.e., passive and then active uptake, for all three metals. The biosorption kinetic data of three tested metals can be effectively simulated by pseudo-second-order rate equations. The pseudo-second-order rate equations provided excellent correlation for these kinetic behaviors. The kinetic rate constants $k_{2ad}$ of pseudo-second-order model for Cd, Ni and Zn biosorption are 0.307, 0.076 and 0.379 g mg$^{-1}$ min$^{-1}$; the $q_c$ are 2.273, 0.885 and 0.769 mg g$^{-1}$, respectively. Metal biosorption fitted well to the Freundlich isotherm. The capacity constants $k$ of the Freundlich model for Cd, Ni and Zn are 0.50, 0.23 and 0.41; the affinity constants $1/n$ are 0.96, 0.81 and 0.31, respectively. Additionally, precipitation behaviours of metals obviously should be carefully examined during biosorption batch tests with activated sludge; otherwise the biosorption effect could be significantly over estimated. All three tested metals, zinc, cadmium and nickel, demonstrated two stages of adsorption on sludge from a continuous-flow biological nutrient removal (BNR) pilotplant. When sludge mixed liquor from the activated sludge system are utilized as absorbent for metal removal, overestimating the isotherm constants is apparently possible if precipitation effects of metals is not isolated during biosorption batch tests [54].

Biosorption of Cu(II) ions onto pre-treated powdered waste sludge (PWS) was investigated using a completely mixed reactor operating in fed-batch mode. Experiments were performed with PWS of different particle sizes between 53 and 231 mm while the feed flow rate (0.25 l h$^{-1}$), feed copper ion
concentrations (200 mg l⁻¹) and the amount of adsorbent (2.0 g PWS) were constant. Breakthrough curves describing variations of the aqueous phase copper ion concentrations with time were determined for different particle sizes of the adsorbent. Percent copper removal from the aqueous phase and the biosorbed copper ion concentrations increased with decreasing particle size or increasing surface area of the PWS. A modified Bohart-Adams equation was used to determine the biosorption capacity of PWS and the rate constant for Cu(II) ion biosorption. The biosorption capacity of PWS based on per unit mass of PWS increased with decreasing particle size due to increased external surface area of PWS. The biosorption capacity of PWS for Cu(II) ions in completely mixed fed-batch reactor was found to be comparable with the powdered activated (PAC) adsorption columns. However, the adsorption rate constant in a completely mixed fed-batch reactor was an order of magnitude larger than those obtained in adsorption columns because of the elimination of mass transfer limitations encountered in the column operations. Therefore, it was proven that the adsorption capacity and the rate of adsorption can be improved by reducing the particle size of the adsorbent (PWS) and using a completely mixed fed-batch reactor due to a larger adsorbent surface area and better contact between the phases. A completely mixed tank operating in fed-batch mode was used for biosorption of Cu(II) ions onto pre-treated powdered waste sludge (PWS) instead of an adsorption column. Fed-batch experiments were performed with different adsorbent (PWS) particle sizes between 53 and 231 mm at constant feed flow rate (0.25 l h⁻¹), feed Cu(II) ion concentration (200 mg l⁻¹) and the amount of PWS (2.0 g). Break-through curves were obtained for each particle size. Percent copper ion removal from the feed solution increased and the effluent Cu(II) ion concentrations decreased with decreasing particle size due to larger binding sites or external surface area of the PWS at small particle sizes. Biosorbed (solid phase) copper ion concentrations (mg g⁻¹) increased with decreasing particle size again due to availability of larger binding sites or surface area of the PWS at small particle sizes. A modified Bohart-Adams equation was used to correlate the break-through time (t_b) with the particle size of the adsorbent. Experimental data obtained at different particle sizes were used to determine.
the constants of the modified Bohart-Adams equation. The surface and the mass adsorption capacities of the PWS were determined along with the adsorption rate constant. The mass adsorption capacity of PWS decreased with increasing particle size while the surface adsorption capacity was constant. The mass adsorption capacity of PWS was comparable with those obtained with the activated carbon in adsorption columns and superior to some of the other adsorbents reported in literature. The adsorption rate constant determined in our study was an order of magnitude larger than those obtained in adsorption column studies using powdered activated carbon (PAC) due to elimination of mass transfer limitations encountered in adsorption columns. A completely mixed adsorption reactor operated in fed-batch mode was proven to be more advantageous as compared to the adsorption columns [196].

An investigation was undertaken to determine the removal of heavy metals (Cd\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\) and Zn\(^{2+}\)) of high environmental priority, due to their toxicity from dilute aqueous solutions by biosorption using inexpensive biomaterials like activated sludge. Each experiment was performed over a period of time to determine the biosorption of heavy metals from the aqueous phase to the solid phase. The maximum sorption uptake of the studied metal ions by activated sludge showed the following order: Cd\(^{2+}\) > Cu\(^{2+}\) > Ni\(^{2+}\) > Zn\(^{2+}\). The pseudo-first and second-order kinetic models were used to describe the kinetic data. Sorption of metal ions from activated sludge follows a pseudo second-order reaction model and the mechanism followed is that of the intraparticle diffusion model. Other models were also reviewed. Quantification of metal-biomass interactions, nature of adsorption, kinetics, ion-exchange as well as models used to characterize activated sludge biosorption were reviewed. All solutions were analyzed using inductively coupled plasma (ICP). The results obtained indicate that it is possible to design a continuous process for waste water treatment by bioadsorbing the ions, followed by sludge regeneration and metal ion recovery. The experimental study would be quite useful in developing an appropriate technology for the removal of heavy metal ions from contaminated industrial effluents.
The waste distillery sludge from sugar-cane industry was pretreated physically (boiled, heated and autoclaved) as well as chemically (HCl, H2SO4, H3PO4, NaOH, Ca(OH)2, Al(OH)3, C6H6, HCHO, CH3OH and C12 H250S03Na (sodium dodecyl sulphate (SDS)) for assessing the comparative sorption capacity of untreated and modified distillery sludge for Pb(II) biosorption from aqueous solutions. Experiments were conducted in shake flasks on a batch basis to access the effect of different experimental parameters such as pH, biosorbent dosage, biosorbent size, initial Pb(II) concentration and contact time. The sorption of Pb(II) ions rapidly occurred within first 30 min followed by slow diffusion controlled step till the equilibrium was reached. The uptake capacity ‘q’ (mgg^-1) of untreated and pretreated distillery sludge was in following order: NaOH (51.29±1.21) > HCl (49.82±1.22) > HCHO (49.56±1.14) > H2SO4 (47.71±1.20) > HgCl2 (45.32±1.06) > Ca(OH)2 (44.01±1.18) > MeOH (43.73±1.23) > C6H6 (42.72±1.19) > H3PO4 (42.01±1.17) > SDS (40.87±1.27) > autoclaved (40.23±1.24) > Boiled (39.95±1.19) > heated (38.87±1.32) > Al (OH)3 (38.30±1.14) > untreated (37.76±1.21). In further parameter studies, the optimized biosorbent size was 0.250 mm at pH 5.0 and best dose was 0.05 g of biosorbent. The applicability of the Langmuir and Freundlich models for sorption process was tested and best fitted model was Langmuir with the coefficient of determination (r^2) value, 0.97, the process followed second order kinetic mechanism. This work illustrated an alternative solution for the management of the distillery sludge (an industrial waste and unwanted biological material) as biosorbent for the removal of Pb(II) from aqueous streams [179].

This study focuses on adsorption of Pb(II) and Hg(II) on nonviable activated sludge biomass at both batch and continuous-flow operational conditions. The raw biomass was supplied from a nearby municipal wastewater treatment plant activated sludge aeration unit. Optimum pH for Pb(II) and Hg(II) were found to be 3.5 and 5.8, respectively. Successively raw biomass was conditioned by 12 different methods and the method yielding highest adsorption capacity, at the predetermined optimum pHs, was investigated for sorption kinetics and isotherm modeling. Among the methods tested, the type of biosolids conditioned by holding the biosolids in NaOH...
solution for 15 min followed by autoclaving at 18 psi at 121°C for 30 min (Type 4) yielded the highest biosorption capacity. The sorption kinetics and isotherm model fitting studies, applying pseudo-first and second order rate models as well as long-familiar Langmuir and Freundlich isotherm models, demonstrated that data fit well to pseudo-second order kinetics and Langmuir isotherm models. The highest adsorption equilibrium, optimum pH and temperature for Pb(II) were 0.387 mmol g⁻¹ at 1.206 mm initial concentration test run at pH of 3.5 and 30°C while the same parameters for Hg(II) were found out to be 0.097 mmol g⁻¹ at 0.099 mM initial concentration test run at pH of 5.8 and 20°C, respectively. Continuous-flow tests were conducted in downflow operational mode using immobilized filter-matrix and the resulting data fitted well to Thomas kinetics model. The high adsorption rate of metal ions at relatively high initial metal ion concentration test runs can be attributed to the higher driving force resulting from the differences between the initial and equilibrium metal ion concentrations in solution-suspension. The high adsorption rate of metal ions at relatively high temperature test runs can be attributed to the decreased liquid viscosity which may give rise to facilitated motion and resultant capture of the ions. Isotherm model fitting tests displayed that Langmuir isotherm gives a better fit for the equilibrium data for both metal ions. Thomas model is quite useful to predict the adsorption capacity of a biomass-matrix column [127].

Two materials were produced from sewage sludge by pyrolysis of dried sewage sludge (PS) and chemical activation of dried sewage sludge with ZnCl₂ followed by pyrolysis (AS). The aim was to study the application of these materials for metal purification from water and to determine the efficiency of each material. The AS carbon showed higher development of the BET surface area (472 m² g⁻¹) and larger volume of pores than the PS. Although AS displayed higher capacity, both PS and AS were able to absorb these metals and the preferential order was equal: Hg(II) > Pb(II) > Cu(II) > Cr(III)). For each metal–adsorbent pair, metal adsorption was highly pH dependent. In all cases the equilibrium was well described both by the Langmuir and the Freundlich isotherms. Furthermore, the corresponding parameters indicate favorable adsorption in all cases. At the corresponding
optimum pH, AS showed the following adsorption capacities: 175.4, 64.1, 30.7 and 15.4 mg g\(^{-1}\) of Hg(II), Pb(II), Cu(II) and Cr(III) respectively. These results indicate the potential application of these sewage sludge based adsorbents for the treatment of metal polluted effluents. Both Langmuir and Freundlich isotherm models describe appropriately he adsorption equilibrium of Hg(II), Pb(II), Cu(II) and Cr(III) onto PS and AS. Desorption studies showed important differences between metals and sorbents. Pb(II) showed very low desorption levels both from PS and AS (around 1%) while Cu(II) desorption from both these adsorbents was over 55% [210].

In the present work, the abilities of sewage sludge and pomace ashes to remove copper (Cu\(^{2+}\)) ions from aqueous solutions were compared. Batch adsorption experiments were performed in order to evaluate the removal efficiency of these materials. Effect of contact time, solution pH, ash concentration and temperature on the removal of Cu\(^{2+}\) was investigated. The results of batch equilibrium studies showed that the solution pH was the key factor affecting the adsorption characteristics. In general, the amount of Cu adsorbed increases as solid concentration and pH increase, and sharply reaches a 99% removal at pH 7.2, then it remains constant over a wide pH region. The marked Cu(II) removal was observed in the acid to neutral region, which can be attributed to the concurrent of Cu(OH)\(_2\) (s) precipitation and the adsorption reactions. In the region of pH 3.0–5.0, the Cu(II) removal is controlled by the adsorption and the major cationic copper adsorbed would be Cu\(^{2+}\). The adsorption test of applying sewage sludge and pomace ashes into synthetic waste water revealed that the adsorption data of these materials for copper ions were better fitted to the Langmuir isotherm, since the correlation coefficients for the Langmuir isotherm were higher than that for the Freundlich isotherm. The estimated maximum capacities of copper adsorbed by sewage sludge and pomace ashes were 5.71 and 6.98 mg g\(^{-1}\), respectively. Experimental results indicated that the adsorption was favorable at higher pH and higher temperature. The adsorption capacity, however, is not highly affected by temperature in the range 10–40°C. Values of \(\Delta G\) ranging from - 4.64 to - 5.13 kcal mol\(^{-1}\) for sewage sludge ash and from - 4.97 to - 5.53 kcal mol\(^{-1}\) for pomace ash suggested that the adsorption reaction is a physical
process enhanced by the electrostatic effect. The values of $\delta_1$ and $\delta_2$ are, respectively, 4.27 kcal mol$^{-1}$ and 30.6 cal K$^{-1}$ mol$^{-1}$ for sewage sludge ash and 4.33 kcal mol$^{-1}$ and 31.3 cal K$^{-1}$ mol$^{-1}$ for pomace ash. The mechanisms of copper removal by these materials included adsorption and precipitation. The sewage sludge and pomace ashes are shown to be effective adsorbents for this metal. The present study aimed to investigate the ability of sewage sludge and pomace ash in the removal of Cu(II) from aqueous solutions. The equilibrium adsorption could be described by Langmuir adsorption isotherm. The sewage sludge and pomace ashes adsorption capacities of Cu(II) range from 5.71 to 6.98 mg g$^{-1}$ and was affected by the pH. The experimental studies showed that sewage sludge and pomace ashes could be used as an alternative, inexpensive and effective material to remove high amount of toxic Cu (II) ions from wastewaters [43].

Activated sludge was obtained from Tehran municipal wastewater treatment plant and was dried and pretreated with three different solutions (H$_2$O$_2$, NaOH and ethanol). The capability of using untreated and pretreated DAS for biosorption of Cd(II) were examined, including equilibration time, effect of initial Cd(II) concentration, kinetic and isotherm studies. Experimental data was shown that most of the Cd(II) ions were sequestered from solution within 60 min and no considerable increase in biosorbed Cd(II) ions after 60 min occurred. Initial Cd(II) ion concentration affected the biosorption as mg g$^{-1}$ at constant DAS concentration. The equilibrium adsorption capacities increase with increasing of initial metal ion concentration for all types of DAS. As the Cd(II) ion concentration increased, more binding sites on DAS were occupied by Cd(II) ions yielding larger biosorbed Cd(II) as mg g$^{-1}$. Biosorption capacity of different types of DAS to remove Cd (II) ions was investigated as a function of Cd(II) concentrations at variable initial Cd(II) concentrations between 10 and 500 mg l$^{-1}$ with a DAS particle size 0.2-0.3 mm using batch biosorption experiments. The maximum biosorption capacity was given 256.41, 217.39, 212.77 and 204.08 mg g$^{-1}$ for the H$_2$O$_2$, NaOH; Ethanol pretreated and untreated DAS, respectively. Among the three different pretreatment solutions, H$_2$O$_2$ was found to be more suitable than untreated DAS and the other pretreated DAS (NaOH and ethanol) that yielding higher
Cd(II) biosorption capacity. The pseudo-second order kinetic model was found to be more suitable than the pseudo-first order kinetic model to correlate the experimental data for all types of DAS ($r^2>0.9$). The Freundlich isotherm was found to fit the experimental data slightly better than the Langmuir isotherm model for all pretreated and untreated DAS. Although the Langmuir isotherm model correlated obtained experimental data reasonably well [233].

Biological treatment of synthetic wastewater containing Cu(II) ions was realized in an activated sludge unit with pre-adsorption of Cu(II) onto powdered waste sludge (PWS). Box-Behnken experimental design method was used to investigate Cu(II), chemical oxygen demand (COD) and toxicity removal performance under different operating conditions. The independent variables were the solids retention time (SRT, 5–30 d), hydraulic residence time (HRT, 5–25 h), feed Cu(II) concentration (0–50 mg l$^{-1}$) and PWS loading rate (0–4 g h$^{-1}$) while percent Cu(II), COD, toxicity (TOX) removals and the sludge volume index (SVI) were the objective functions. The data were correlated with a quadratic response function ($r^2 = 0.99$). Cu(II), COD and toxicity removals increased with increasing PWS loading rate and SRT while decreasing with the increasing feed Cu(II) concentration and HRT. Optimum conditions resulting in maximum Cu(II), COD, toxicity removals and SVI values were found to be SRT of 30 d, HRT 15 h, PWS loading rate 3 g h$^{-1}$ and feed Cu(II) concentration of less than 30 mg l$^{-1}$ [197].

Wine-processing waste sludge (WPWS) has been shown to have powerful potential for sorption of some heavy metals (i.e., chromium, lead and nickel) in single-component aqueous solutions. But although most industrial wastewater contains two or more toxic metals, there are few sorption studies on multi-component metals by WPWS. The study had two goals: firstly conduct competitive adsorption using Cr, Cu and Zn as sorbates and examine their interaction in binary or ternary systems; and secondly to determine the effects of temperature on the kinetic sorption reaction. The sludge tested contained a high amount of organic matter (38%) and had a high cation exchange capacity (CEC, 255 cmolc kg$^{-1}$). Infrared analysis reveals that carboxyl is the main functional group in this WPWS. The 13C NMR determination indicates alkyl-C and carboxyl-C are major organic functional
groups. At steady state, there are about 40.4% (Cr), 35.0% (Cu) and 21.9% (Zn) sorbed in the initial 6.12mM of single-component solutions. Only pseudo-second-order sorption kinetic model successfully describes the kinetics of sorption for all experimental metals. The rate constants, $K_2$, of Cr, Cu and Zn in single-component solutions are 0.016, 0.030 and 0.154 g mg$^{-1}$ min$^{-1}$, respectively. The sorption of metals by WPWS in this competitive system shows the trend: Cr > Cu > Zn. Ions of charge, hydrated radius and electronic configuration are main factors affecting sorption capacity. The least sorption for Zn in this competitive system can be attributed to its full orbital and largest hydrated radius. Though the effect of temperature on Zn sorption is insignificant, high temperature favors the other metallic sorptions, in particular for Cr. However, the Cr sorption is lower than Cu at 10°C. The Cr sorption by WPWS can be higher than that of Cu at 30°C and 50°C. This study of single-component aqueous solutions has shown wine-processing waste sludge to be an effective sorbent for removing Cr, Cu and Zn in aqueous solutions. Nevertheless, the Zn sorptions in mixture solutions are suppressed significantly by competition with others [149].

This work presents results of kinetic and equilibrium studies for the removal of heavy metals (Cr, Cu, Cd, Ni and Pb) from the sewage sludge, using a new technique of solid–liquid–solid extraction with the adsorption–diffusion column filled by the zeolite. Extraction (sorption) of the heavy metals by the clinoptilolite from aqueous solution of the clinoptilolite and the sewage sludge composition is characterized by three clearly defined stages: the first stage of intensive extraction, the second stage of inversion with prevalence of the metals desorption, and the third stage of stabilization with the moderate extraction increase and attainment of steady state. The highest extraction of the metals has been observed during the first stage. The rate coefficients estimated by pseudo-second-order kinetic and intraparticle diffusion models during the first stage are 5–10 times more than the same during the third stage. Efficiency of the metal uptake by the clinoptilolite evaluated in the equilibrium study grows with increase of the zeolite dose added to the sewage sludge. Addition of 25% of the zeolite provides extraction efficiency of cadmium and lead of about 84%, chromium, copper and nickel of 66%, 61%
and 50% relatively. Both the rate constants and the distribution coefficients values grow with increase in the added clinoptilolite dose. The distribution coefficient values suggest the following selectivity series of the zeolite: Cd > Pb > Cr > Cu > Ni. Application of the clinoptilolite previously treated by 2M NaCl, 2M HCl solutions and by ultrasound demonstrates the biggest effect of 30 min ultrasound treatment on the clinoptilolite extraction ability. The estimated values of $\Delta G$ show that the heavy metal extraction by the clinoptilolite should be considered as a physical adsorption. According to the added zeolite amounts Gibbs energy of extraction varies in the range of 19–44, 14–49, 8–15, 16–20 and 7–10 kJmol$^{-1}$ for Pb, Cd, Cu, Cr, Ni. The negative values testify to an exothermic nature of the extraction process. The difference between energetic potentials of the components is a driving force of the metal redistribution in the system “clinoptilolite–water–sludge. According to the added zeolite amounts the distribution coefficients of lead, cadmium, chromium, copper and nickel vary in the range of 8–18, 6–20, 7–8, 3–6 and 3–4, respectively. In this case the efficiency of uptake of Pb, Ni, Cd, Cu and Cr increase for 14%, 10%, 7%, 6% and 4% relatively [234].

This work investigates the chemical mechanisms operating in cadmium and lead removal by activated sludge in sequencing batch reactors. Selective extraction and acid digestion of sludge samples denoted that both Cd and Pb are mainly present as surface-bound metals. Characterization of sludge samples by potentiometric titrations and IR spectra suggested that carboxylic and amino groups are the main active sites responsible for the binding properties of the biomass. Simulation of metal speciation implemented with complexation constants determined in biosorption tests, showed that cadmium predominates as biosorbed species, while lead was mainly removed by precipitation. Experimental data and theoretical analyses reported in this work proposed an original methodological approach to isolate and quantify metal-sludge interactions depending on both metal solution chemistry and sludge sites. In particular using two heavy metals generally present in waste waters, one with low solubility in the range of investigated conditions, it was possible to quantify the different mechanisms involved in their removal by independent experimental tests (selective extractions, acid digestions,
potentiometric titrations, IR, isotherms) and their modelling (mechanistic titration modeling and Langmuir isotherms). Indeed, according to the mechanism predominating in metal removal different extractive procedures can also be attempted for the recovery of specific metals. This methodological approach can guide further treatment and disposal of sludge coming from the treatment of metal-bearing effluents as a function of the specific metal and range of concentration [190].

Batch experiments were conducted to remove Cr(VI) from aqueous solution using activated sludge biomass. The effects of acid pretreatment of the biomass, initial pH, biomass and Cr(VI) concentrations on its removal efficiency were investigated. Proton consumption during the removal process and the reducing capacity of sludge biomass were studied. The results showed that acid pretreatment significantly improved removal efficiency and increase reducing capacity by 20.4% of Cr(VI). The Cr(VI) reducing capacity of the raw sludge biomass was about three times higher than that of FeSO₄·7H₂O. The removal was remarkably pH-dependent; lower pH (pH = 1, 2) facilitated Cr(VI) reduction while higher pH (3 & 4) favored sorption of the converted Cr(III). Lower Cr(VI) concentration as well as higher biomass concentration accelerated Cr(VI) removal. Cr(VI) reduction was not the only reason for proton consumption in the removal process. Sorption as well as hydrolysis of the converted Cr(III) may also play an important role in pH fluctuation. Kinetic models based on reduction reaction could not describe the experimental data well, while the pseudo-second-order adsorption model fitted quite well with the data except under higher pH conditions (pH = 3, 4). Activated sludge biomass has proved to be a promising biosorbent, as well as an organic reductant, for Cr(VI) removal from aqueous environment. The mechanisms of Cr(VI) removal involved sorption and reduction of Cr(VI). Acid pretreatment of sludge biomass could successfully remove most of hydrogen ions consuming substances and supply comparatively stable acid environment which facilitated Cr(VI) removal [281].

In this work, the removal of lead and cadmium from an aqueous solution by a local dairy sludge was investigated in a batch system. Biosorption of these heavy metals was studied as a function of solution initial
pH, equilibrium time, temperature, biosorbent dose, biosorbent particle diameter and initial metal ion concentration. Maximum sorption was observed at a pH value of 5.0 and a temperature of 40°C. Equilibrium uptake increased with increasing metal ion concentration for both metals with a maximum sorption capacity of a 148.6 mgg⁻¹ for Pb(II) and 66.7 mgg⁻¹ for Cd(II). The Langmuir model was found to better describe the sorption of lead ions with a correlation factor of 0.99 while Freundlich and Temkin models were better for Cd(II) sorption. The temperature increase from 20°C to 40°C enhanced the uptake of Pb(II) by 20% and Cd(II) by 5%. The lower values of $r^2$ show that the biosorption of lead is not well described by the Freundlich isotherm especially at higher concentration (100 mg l⁻¹). The biosorption kinetics for the metal ions studied at different initial solutions concentrations, dairy sludge loadings and particle diameter were best described using pseudo-second order suggesting a chemical process for the mechanism of biosorption between the metal ions and the sorbent. SEM micrographs were determined before and after sorption. The tests of desorption showed that up to 76.6% of Pb(II) were recovered by HNO₃ (0.3 M) and 62.5% of Cd(II) by HCl (0.1 M). This study shows that this dairy sludge as a solid waste can be used as an alternative to cleanse heavy metal laden industrial wastewater [221].

The biosorption potential of dried activated sludge as a biosorbent for zinc(II) removal from aqueous solution was investigated. The effects of initial pH, contact time, initial zinc ion concentration, and adsorbent dosage on the biosorption processes were determined. The zinc adsorption capacity increased with increase in pH values ranging from 2 to 5. The extent of zinc removal was directly related with the dosage of the dried activated sludge in the solution. The zinc removal efficiency increased from 7.5% to 43.7% with increase in adsorbent dosage from 0.5 to 3.0 g l⁻¹ at an initial zinc ion concentration of 100 mg l⁻¹. The uptake of zinc ions by the dried activated sludge increased from 8.9 to 17.6 mgg⁻¹, and the zinc removal efficiency decreased from 89.0% to 17.6% when the initial zinc ion concentration increased from 20 to 200 mg l⁻¹. The equilibrium data were modeled by the Langmuir and Freundlich isotherms. The Langmuir isotherm model ($r^2 = 0.999$) was proved to fit the equilibrium data much better than the Freundlich
isotherm model ($r^2 = 0.918$). The monolayer adsorption capacity of dried activated sludge for zinc(II) was found to be 17.86 mg g$^{-1}$ at pH of 5 and 25°C. The kinetic data were tested using pseudo-first and second-order models. The results suggested that the pseudo second-order model ($r^2 > 0.999$) was better for the description of the adsorption behavior of zinc(II) onto the dried activated sludge. The FT-IR spectral analysis indicated that amide group was mainly responsible for zinc(II) removal and that hydroxide group was also involved in zinc(II) binding to some degree. Based on these results, it can be concluded that as a low-cost biosorbent, the dried activated sludge, can be used for zinc(II) ions removal from aqueous solutions [286].

Due to high solubilization of organic matter, classical sorption models were not able to correctly describe the equilibrium of heavy metals uptake by activated sludge after disintegration processes. A new semi-mechanistic model deriving from the simple Freundlich equation was developed in this study to describe metal interactions within activated sludge previously subjected to ultrasonic treatment: the equilibrium between both aqueous (complexation with soluble/colloidal organic matter released during the treatment) and particulate (sorption on sludge flocs, precipitation) metal fractions was modeled. The results of biosorption and precipitation tests were described by the new model. This allowed a better understanding of the influence of activated sludge properties (surface functional groups, structure, chemical composition) on the fate of both copper and cadmium in sonicated activated sludge. It was initially set up to allow the qualitative and quantitative description of heavy metals sorption onto activated sludge pretreated by physical, thermal or chemical methods in the field of excess sludge production reduction. The use of this model yielded information about metal uptake capacity by sludge particulates (parameter n) as well as metal affinity towards sludge particulates (parameter F) and soluble organic matter (parameter K). The degree of metal uptake by sludge particulates was found to be dependent on the evolutions of metal interaction mechanisms after sonication. Both cadmium and copper uptake capacities increased due to several reasons: the decrease of floc size offered an extended surface area, the increase of the relative proportions of negatively charged (at pH 7.0) groups provided more
surface binding sites, the increase of soluble $\text{PO}_4^{3-}$ concentration favored metal precipitation. However, copper uptake was at the same time limited by soluble complexation with the released organic matter: this was well described by the model which considered both DOC concentration and metal affinity with this organic matter ($K$); this affinity was higher for the matter released during sonication than for the original wastewater dissolved compounds in untreated sample. The use of this model constituted of a useful tool for understanding and predicting heavy metals behaviour in wastewater treatment plants when excess sludge reduction processes are introduced. This field of research is indeed of great concern since the sustainability of excess sludge reduction processes partly relies on the fate of micropollutants such as heavy metals. This study also opens opportunities to investigate the fate of metallic elements and other micropollutants in relation with activated sludge and process characteristics [145].

The biosorption characteristics of cations and anions from aqueous solution using modified aerobic granules were investigated. Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) analysis exhibit the presence on the granule surface. Compared with the raw granule, the modified aerobic granules showed a significant increase in sorption capacity for both metal ions. The monolayer biosorption capacity of granules for Cu(II) and Cr(VI) ions was found to be 71.239 and 348.125 mg/g. Solution pH played an important role in the metal ions biosorption onto modified aerobic granules. The optimum solution pH for adsorption of Cu(II) and Cr(VI) from aqueous solutions was found to be 6.0 and 5.2, respectively. The biosorption data fitted better with the Redlich–Peterson isotherm model. FTIR and XPS reveal that carboxyl and amide groups on the biomass surface were involved in the sorption of copper and chromium and complexation dominated the sorption process. Moreover, XPS analysis indicates redox reaction also takes place in solution or on the biomass surface. This study concluded that PEI grafted aerobic granules are an appropriate adsorbent for removing metal ions from wastewater [238].