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Chapter 7

Determination of Trace Metals in Waste Water and Their Removal Processes

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1. Introduction

Since the second part of 20th century, there has been growing concern over the diverse effects of heavy metals on humans and aquatic ecosystems. Environmental impact of heavy metals was earlier mostly attributed to industrial sources. In recent years, metal production emissions have decreased in many countries due to strict legislation, improved cleaning/purification technology and altered industrial activities. Today and in the future, dissipate losses from consumption of various metal containing goods are of most concern. Therefore, regulations for heavy metal containing waste disposal have been tightened [1].

A significant part of the anthropogenic emissions of heavy metals ends up in wastewater. Major industrial sources include surface treatment processes with elements such as Cd, Pb, Mn, Cu, Zn, Cr, Hg, As, Fe and Ni, as well as industrial products that, at the end of their life, are discharged in wastes. Major urban inputs to sewage water include household effluents, drainage water, business effluents (e.g. car washes, dental uses, other enterprises, etc.), atmospheric deposition, and traffic related emissions (vehicle exhaust, brake linings, tires, asphalt wear, gasoline/oil leakage, etc.) transported with storm water into the sewerage system. For most applications of heavy metals, the applications are estimated to be the same in nearly all countries, but the consumption pattern may be different. For some applications which during the last decade has been phased out in some countries, there may, however, today be significant differences in uses [2-4].

Most common sources of heavy metals to waste and/or waste water are [1]; (i) Mining and extraction; by mining and extraction a part of the heavy metals will end up in tailings and other waste products. A significant part of the turn over of the four heavy metals with mining waste actually concerns the presence of the heavy metals in waste from extraction of other metals like zinc, copper and nickel. It should, however, be kept in mind that mining waste is generated in-
dependent of the subsequent application of the heavy metal. (ii) Primary smelting and processing; a minor part of the heavy metals will end up in waste from the further processing of the metals. (iii) Use phase; a small part of the heavy metals may be lost from the products during use by corrosion and wear. The lost material may be discharged to the environment or end up in solid waste either as dust or indirectly via sewage sludge. (iv) Waste disposal; the main part of the heavy metals will still be present when the discarded products are disposed off. The heavy metals will either be collected for recycling or disposed of to municipal solid waste incinerators (MSWI) or landfills or liquid waste. A minor part will be disposed of as chemical waste and recycled or landfilled via chemical waste treatment. (v) vulcanic erruptions. (vi) fossil fuel combustion. (vii) agriculture (viii) erosions (ix) metallurgical industries. Actually metal pollutants are neither generated nor completely eliminated; they are only transferred from one source to another. Their chemical forms may be changed or they are collected and immobilized not to reach the human, animals or plants.

The term heavy metal has never been defined by any authoritative body such as The International Union of Pure and Applied Chemistry (IUPAC). It has been given such a wide range of meanings by different authors that it is effectively meaningless. No relationship can be found between density (specific gravity) and any of the various physicochemical concepts that have been used to define “heavy metals” and the toxicity or ecotoxicity attributed to heavy metals. The term bioavailability is more appropriate to define the potential toxicity of metallic elements and their compounds. Bioavailability depends on biological parameters as well as the physicochemical properties of metallic elements, their ions, and compounds. These in turn depend upon the atomic structure of the metallic elements. Thus, any classification of the metallic elements to be used in scientifically based legislation must itself be based on the periodic table or some subdivision of it. In conclusion, heavy metals commonly used in industry and generically toxic to animals and to aerobic and anaerobic processes, but all of them are not dense nor entirely metallic. Includes As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Zn. All of them pose a number of undesired properties that affect humans and the environment [5].

Effluents from textile, leather, tannery, electroplating, galvanizing, pigment and dyes, metallurgical and paint industries and other metal processing and refining operations at small and large-scale sector contain considerable amounts of toxic metal ions [4]. The toxic metals and their ions are not only potential human health hazards but also to another life forms. Toxic metal ions cause physical discomfort and sometimes life-threatening illness including irreversible damage to vital body system [6]. From the eco-toxicological point of view, the most dangerous metals are mercury, lead, cadmium and chromium(VI). In many instances, the effect of heavy metals on human is not well understood. Metal ions in the environment bioaccumulate and are biomagnified along the food chain. Therefore, their toxic effect is more pronounced in animals at higher trophic levels. Mine tailing and effluents from non-ferrous metals industry are the major sources of heavy metals in the environment. Among commonly used heavy metals, Cr(III), Cu, Zn, Ni and V are comparatively less toxic then Fe and Al. Cu is mainly employed in electric goods industry and brass production. Major applications for Zn are galvanization and production of alloys. Cadmium has a half-life of 10–30 years and its accumulation in human body affects kidney, bone and also causes cancer and its use is increasing in industrial applica-
tions such as electroplating and making pigments and batteries. Chromium compounds are nephrotoxic and carcinogenic in nature. As a result of increasing awareness about the toxicity of Hg and Pb, their large-scale use by various industries has been either curtailed or eliminated. An effluent treatment facility within the industry discharging heavy metals contaminated effluent will be more efficient than treating large volumes of mixed wastewater in a general sewage treatment plant. Thus it is beneficial to devise separate treatment procedures for scavenging heavy metals from the industrial wastewater [4, 6, 7].

The analysis of wastewater for trace and heavy metal contamination is an important step in ensuring human and environmental health. Wastewater is regulated differently in different countries, but the goal is to minimize the pollution introduced into natural waterways. In recent years, metal production emissions have decreased in many countries due to heavy legislation, improved production and cleaning technology. A variety of inorganic techniques can be used to measure trace elements in waste water including flame atomic absorption spectrometry (FAAS) and graphite furnace (or electrothermal) atomic absorption spectrometry (GFAAS or ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Depending upon the number of elements to be determined, expected concentration range of analytes and the number of samples to be run, the most suitable technique for business requirements can be chosen.

Several industrial wastewater streams may contain heavy metals such as Sb, Cr, Cu, Pb, Zn, Co, Ni, etc. The toxic metals, existing in high or even in low concentrations, must be effectively treated/removed from the wastewaters. Among the various treatment methods applied to remove heavy or trace metals, chemical precipitation process has been the most common technology. The conventional heavy metal removal process has some inherent shortcomings such as requiring a large area of land, a sludge dewatering facility, skillful operators and multiple basin configuration. In recent years, some new processes such as biosorption, neutralization, precipitation, ion exchange, adsorption etc. have been developed and extensively used for the heavy metal removal from wastewater.

In this chapter the novel and common methods for the determination of trace heavy metals in waste water and their removal processes are explained.

2. Toxicity effects of some heavy metals in the wastewater [1, 3, 5]

All heavy metals are effected to human and environment by different ways. For example; lead in the environment is mainly particulate bound with relatively low mobility and bioavailability. Lead does, in general, not bioaccumulate and there is no increase in concentration of the metal in food chains. Lead is not essential for plant or animal life. Of particular concern for the general population is the effect of lead on the central nervous system. Lead has been shown to have effects on haemoglobin synthesis and anaemia has been observed in children at lead blood levels above 40 µg/dl. Lead is known to cause kidney damage. Some of the effects are reversible, whereas chronic exposure to high lead levels may result in continued decreased kidney function and possible renal failure. The evidence for carcinogenici-
ty of lead and several inorganic lead compounds in humans is inadequate. Classification of The International Agency for Research on Cancer (IARC) is class 2B which is the agent (mixture) is possibly carcinogenic to humans. The exposure circumstance entails exposures that are possibly carcinogenic to humans. In the environment, lead binds strongly to particles, such as soil, sediment and sewage sludge. Because of the low solubility of most of its salts, lead tends to precipitate out of complex solutions. It does not bioaccumulate in most organisms, but can accumulate in biota feeding primarily on particles, e.g. mussels and worms. These organisms often possess special metal binding proteins that removes the metals from general distribution in their organism. Like in humans, lead may accumulate in the bones. One of the most important factors influencing the aquatic toxicity of lead is the free ionic concentration and the availability of lead to organisms. Lead is unlikely to affect aquatic plants at levels that might be found in the general environment.

Mercury is a peculiar metal. Most conspicuous is its fluidity at room temperature, but more important for the possible exposure of man and the environment to mercury are two other properties:

1. Under reducing conditions in the environment, ionic mercury changes to the uncharged elemental mercury which is volatile and may be transported over long distances by air.

2. Mercury may be chemically or biologically transformed to methylmercury and dimethylmercury, of which the former is bioaccumulative and the latter is also volatile and may be transported over long distances. Mercury is not essential for plant or animal life. The organic forms of mercury are generally more toxic to aquatic organisms than the inorganic forms. Aquatic plants are affected by mercury in the water at concentrations approaching 1 mg/litre for inorganic mercury, but at much lower concentrations of organic mercury.

Cadmium and cadmium compounds are, compared to other heavy metals, relatively water soluble. They are therefore also more mobile in e.g. soil, generally more bioavailable and tends to bioaccumulate. Cadmium is not essential for plant or animal life. Cadmium is readily accumulated by many organisms, particularly by microorganisms and molluscs where the bioconcentration factors are in the order of thousands. In aquatic systems, cadmium is most readily absorbed by organisms directly from the water in its free ionic form Cd (II). The acute toxicity of cadmium to aquatic organisms is variable, even between closely related species, and is related to the free ionic concentration of the metal. Cadmium interacts with the calcium metabolism of animals. In fish it causes lack of calcium (hypocalcaemia), probably by inhibiting calcium uptake from the water. Effects of long-term exposure can include larval mortality and temporary reduction in growth.

Chromium occurs in a number of oxidation states, but Cr(III) (trivalent chromium) and Cr(IV) (hexavalent chromium) are of main biological relevance. There is a great difference between Cr(III) and Cr(VI) with respect to toxicological and environmental properties, and they must always be considered separately. Chromium is similar to lead typically found bound to particles. Chromium is in general not bioaccumulated and there is no increase in concentration of the metal in food chains. Contrary to the three other mentioned heavy metals, Cr(III) is an essential nutrient for man in amounts of 50 - 200 µg/day. Chromium is nec-
necessary for the metabolism of insulin. It is also essential for animals, whereas it is not known whether it is an essential nutrient for plants, but all plants contain the element. In general, Cr(III) is considerably less toxic than Cr(VI). Cr(VI) has been demonstrated to have a number of adverse effects ranging from causing irritation to cancer. Hexavalent chromium is in general more toxic to organisms in the environment than the trivalent chromium. Almost all the hexavalent chromium in the environment is a result of human activities. Chromium can make fish more susceptible to infection; high concentrations can damage and/or accumulate in various fish tissues and in invertebrates such as snails and worms. Reproduction of the water flea Daphnia was affected by exposure to 0.01 mg hexavalent chromium/litre. Hexavalent chromium is accumulated by aquatic species by passive diffusion. In general, invertebrate species, such as polychaete worms, insects, and crustaceans are more sensitive to the toxic effects of chromium than vertebrates such as some fish. The lethal chromium level for several aquatic and terrestrial invertebrates has been reported to be 0.05 mg/litre.

Copper can be found in many wastewater sources including, printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservatives and printing operations. Typical concentrations vary from several thousand mg/l from plating bath waste to less than 1 ppm from copper cleaning operations. Copper can be found in many kinds of food, in drinking water and in air. Because of that we absorb eminent quantities of copper each day by eating, drinking and breathing. The absorption of copper is necessary, because copper is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of copper, too much copper can still cause eminent health problems. 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 it hardly ever enters groundwater. In surface water copper can travel great distances, either suspended on sludge particles or as free ions [8].

Nickel is a naturally occurring element widely used in many industrial applications for the shipbuilding, automobile, electrical, oil, food and chemical industries. Although it is not harmful in low quantities, nickel is toxic to humans and animals when in high concentrations. Nickel can be present in wastewater as a result of human activities. Sources of nickel in wastewater include ship cruise effluents, industrial applications and the chemical industry [9].

Arsenic is found in wastewater from electronic manufactures making gallium arsenide wafers and electronic devices. It also can be found in silicon semiconductor operations that use high dose arsenic implants. Other sources of arsenic are ground water in agricultural areas where arsenic was once used as an insecticide. Most environmental arsenic problems are the result of mobilization under natural conditions. However, mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides, and crop desiccants and use of arsenic additives to livestock feed create additional impacts. Arsenic exists in the −3, 0, +3 and +5 oxidation states. Each of them have different toxic effect both human and environment.

Actually all chemicals, including even essential elements, drugs and in fact water, are toxic above (and below) their limiting values. However, some elements such as arsenic lead, cadmium, mercury, described as toxic, are known to be toxic for living beings at any concentration and they are not asked to be taken in to the body even in ultratrace levels.
3. Determination Techniques of Heavy Metals in Waste Water Samples

In order to determine the heavy trace metals, there are many inorganic techniques such as FAAS, ETAAS, ICP-OES, ICP-MS as well as anodic stripping and recently laser induced breakdown spectroscopy (LIBS). Each technique has its own advantages and disadvantages which will be discussed in this chapter.

Actually all the steps of an analysis, namely (i) representative sampling, (ii) to prevent analyte loss e.g. its sorption on vessel wall, (iii) contamination from the environment, wares, chemicals added to the sample, (iv) transfer the sample to the lab, (v) treatment of sample prior to analysis (leaching, extraction, preconcentration/separation of the analytes, (vi) choose of the method considering its limitations, (vii) calibration of the vessels, instrument etc, (viii) preparation of sample, all solutions, standards correctly and appropriately, (ix) to test the accuracy of the method using Certified Reference Materials (CRM), (x) evaluation of results statistically and reporting are all the rings of a chain. Each step is important and potential source of error if not applied conveniently. The weakest ring of the chain limits the accuracy and quality of the results. If it is broken, the analysis collapses. Therefore, all the steps of an analysis should be performed with caution. A problem or error even in one of those steps causes the result to be wrong. As in all analyses, sample preparation step is the most important one which should be completed quickly, easy and safely. Waste water samples may contain particulates or organic materials which may require pretreatment before spectrometric analysis. In order to analyze total metal content of a sample, concentration of metals inorganically and organically bound, dissolved or particulated materials should be found.

As stated in Standard Methods, samples which are colorless and transparent, having a turbidity of <1 NTU (Nephelometric Turbidity Unit), no odor and single phase may be analyzed directly or, if necessary, after enrichment by atomic absorption spectrometry (flame or electro thermal vaporization) or inductively coupled plasma spectrometry (atomic emission or mass spectrometry) for metals without digestion. For further verification or if changes in existing matrices are encountered, comparison of digested and undigested samples should be done [10].

If samples have particulates and only the dissolved metals will be analyzed, filtration of sample and analyzing of filtrate will be enough. To be on the safe side, if particulates involved, convenient digestion procedures are suggested. Since different filtration procedures produce different blank values, it is always suggested to study with a blank solution. If only the metal contents of particulates are asked to be determined, then the sample is filtered and the filter is digested and analyzed.

In order to reduce interferences, organic matrix of the sample should be destroyed by digestion as well as metal containing compounds are decomposed to obtain free metal ions which can be determined by atomic absorption spectrometry (AAS) or inductively coupled plasma (ICP) more conveniently. The procedures for destroying organic material and dissolving heavy metals fall into three groups; wet digestion by acid mixtures prior to elemental analysis, dry ashing, followed by acid dissolution of the ash and microwave assisted digestion.
In Standard Methods if metal concentration is around 10-100, it is advised to digest 10 mL of sample. For less metal concentrations, sample volume could be around 100 mL for subsequent enrichment. For most digestion procedures, nitric acid is used which is an acceptable matrix for both flame and electrothermal atomic absorption and ICP-MS. Nitric acid digestion, 100 mL of sample is heated in a beaker with 5 mL concentrated nitric acid. Boiling should be prevented and addition of acid should be repeated till a light colored, clear solution is obtained. Sometimes, if the samples involve readily oxidizable organic matters, mixtures of HNO₃- H₂SO₄ or HNO₃- HCl may be used. Samples with high organic contents, mixtures of HNO₃- HClO₄ or HNO₃-H₂O₂ or HNO₃-HClO₄-HF can be used. The latter is especially important for the dissolution of particulate matter. For samples which have high organic content, dry ashing may be favored. Wet digestion systems are performed either with a reflux or in a beaker on a laboratory hot plate. These methods are temperature limited because of the risk of contaminants from the air, laboratory equipment etc. Also there may be lost of volatile elements (As, Cd, Pb, Se, Zn and Hg etc.). Temperature limitation can be overcome by closed pressure vessels, i.e. microwave digestion. Closed systems allow high pressures above atmosphere to be used. This allows boiling at higher temperatures and often leads to complete dissolution of most samples. In the American Society for Testing and Materials (ASTM) Standards (D1971-11) ‘Standard practices for digestion of water samples for determination of metals by FAAS, ETAAS, ICP-OES or ICP-MS’ for waste water samples it is advised to use, 100 volume of sample: 5 volume HCl: 1 volume HNO₃ is put to microwave digestion vessels for 30 minutes at 121°C and 15 psig. A comparison of digestion techniques is given in Table 1.

| Wet Ashing          | Microwave Digestion | Wet Ashing          | Microwave Digestion |
|---------------------|---------------------|---------------------|---------------------|
| Time Consumption    | Slow                | Rapid               |                     |
| Temperature         | Low                 | High                |                     |
| Pressure            | Atmospheric         | Above Atmospheric   |                     |
| Operator Skills     | High                | Moderate            |                     |
| Safety              | Corrosive-explosive reagents | Corrosive-explosive reagents |         |
| Operating Cost      | Low                 | High                |                     |
| Environmental Effect| High                | Low                 |                     |
| Analyte Loss&Contamination | High               | Low                 |                     |

Table 1. Comparison of Digestion Techniques.

After choosing the effective sample preparation step, most useful techniques were explained below, like atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), laser induced breakdown spectroscopy (LIBS) and anodic stripping.
3.1. Atomic Absorption Spectrometry

Atomic Absorption Spectrometry (AAS) is an analytical method for quantification of over 70 different elements in solution or directly in solid samples. Procedure depends on atomization of elements by different atomization techniques like flame (FAAS), electrothermal (ETAAS), hydride or cold vapor. Each atomization technique has its advantages and limitations or drawbacks. A comparison of several AAS techniques is given in Table 2.

Two types of flame are used in FAAS: (i) air/acetylene flame, (ii) nitrous oxide/acetylene flame. Flame type depends on thermal stability of the analyte and its possible compounds formed with flame concomitants. Temperature formed in air-acetylene flame is around 2300°C whereas acetylene-nitrous oxide (dinitrogen oxide) flame is around 3000°C [15]. Generally with air/acetylene flame antimony, bismuth, cadmium, calcium, cesium, chromium, cobalt, copper, gold, itidium, iron, lead, lithium, magnesium, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, thallium, tin and zinc can be determined. On the other hand for refractory elements such as aluminium, barium, molybdenum, osmium, rhenium, silicon, thorium, titanium and vanadium, nitrous oxide/acetylene flame should be used [10]. But some elements like vanadium, zirconium, molybdenum and boron has lower sensitivity in the determination by FAAS because the temperature is insufficient to break down compounds of these elements. Samples should be in solution form, or digested to be detected by FAAS. Typical detection limits are around ppm range and sample analysis took 10-15 seconds per element [16]. The block diagram of FAAS and GFAAS is depicted in Figure 1.

Generally, hollow cathode lamps as source, flame or graphite furnace as an atomizer, grating as a wavelength selector and photomultiplier as a detector are used.

![Block Diagram for FAAS and GFAAS](image)

Mahmoud et al. determined Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb by FAAS after enrichment with chemically modified silica gel N-(1-carboxy-6-hydroxy) benzylidene propylamine (SiG-CHBPA) [16]. Afkhami et al. determined Cd in water samples after cloud point extraction in Triton X-114 without adding chelating agents [18]. Mohamed et al. determined chromium species based on the catalytic effect of Cr(III) and/or Cr(VI) on the oxidation of 2-amino-5-methylphenol (AMP) with H$_2$O$_2$ by FAAS [19]. Mahmoud et al. pre-concentrated Pb(II) by newly modified three alumina–physically loaded-dithizone adsorbents then determined by FAAS [20]. Cassella et al. prepared a minicolumn packed with a styrene-divinylbenzene resin func-
rounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is nonselective and is highly sensitive to pH of the solution.

Electro-winning is widely used in the mining and metallurgical industrial operations for heap leaching and acid mine drainage. It is also used in the metal transformation and electronics and electrical industries for removal and recovery of metals. Metals like Ag, Au, Cd, Co, Cr, Ni, Pb, Sn and Zn present in the effluents can be recovered by electro-deposition using insoluble anodes.

Electro-coagulation is an electrochemical approach, which uses an electrical current to remove metals from solution. Electro-coagulation system is also effective in removing suspended solids, dissolved metals, tannins and dyes. The contaminants presents in wastewater are maintained in solution by electrical charges. When these ions and other charged particles are neutralized with ions of opposite electrical charges provided by electrocoagulation system, they become destabilized and precipitate in a stable form.

Cementation is a type of another precipitation method implying an electrochemical mechanism in which a metal having a higher oxidation potential passes into solution e.g. oxidation of metallic iron, Fe(0) to ferrous Fe(II) to replace a metal having a lower oxidation potential. Copper is most frequently separated by cementation along with noble metals such as Ag, Au and Pb as well as As, Cd, Ga, Pb, Sb and Sn can be recovered in this manner.

Reverse osmosis and electro-dialysis involves the use of semi-permeable membranes for the recovery of metal ions from dilute wastewater. In electro-dialysis, selective membranes (alternation of cation and anion membranes) are fitted between the electrodes in electrolytic cells, and under continuous electrical current the associated.

Most of these methods suffer from some drawbacks such as high capital and operational costs and problem of disposal of residual metal sludge. Ionexchage is feasible when an exchanger has a high selectively for the metal to be removed and the concentrations of competing ions are low. The metal may then be recovered by incinerating the metal-saturated resin and the cost of such a process naturally limits its application to only the more valuable metals. In many cases, however, the heavy metals are not valuable enough to warrant the use of special selective exchangers/resins from an economic point of view. Cost effective alternative technologies or sorbents for treatment of metals contaminated waste streams are needed. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing required and local availability. In general, a sorbent can be assumed as 'low cost'' if it requires little processing, is abundant in nature, or is a by-product or waste material from another in-
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dustry. Of course improved sorption capacity may compensate the cost of additional processing. This has encouraged research into using low-cost adsorbent materials to purify water contaminated with metals. Another major disadvantage with conventional treatment technologies is the production of toxic chemical sludge and its disposal/treatment is not eco-friendly. Therefore, removal of toxic heavy metals to an environmentally safe level in a cost effective and environment friendly manner assumes great importance.

In light of the above, biological materials and some adsorption materials have emerged as an economic and eco-friendly option. Adsorption is one the physico-chemical treatment processes found to be effective in removing heavy metals from aqueous solutions. According to literature, an adsorbent (sorbent) can be considered as cheap or low-cost if it is abundant in nature, requires little processing and is a byproduct of waste material from waste industry [66-68, 76-78].

Of course improved sorption capacity may compensate the cost of additional processing. Some of the reported low-cost sorbents such as bark/tannin-rich materials, lignin, chitin/chitosan, dead biomass, seaweed/algae/alginate, xanthate, zeolite, clay, fly ash, peat moss, bone gelatin beads, leaf mould, moss, iron-oxide-coated sand, modified wool and modified cotton. Important parameters for the sorbent effectiveness are effected by pH, metal concentration, ligand concentration, competing ions, and particle size [4, 66-68].

Another type of sorbent is plant waste [68]. Plant wastes are inexpensive as they have no or very low economic value. Most of the adsorption studies have been focused on untreated plant wastes such as papaya wood, maize leaf, teak leaf powder, lalang (Imperata cylindrica) leaf powder, rubber (Hevea brasiliensis) leaf powder, Coriandrum sativum, peanut hull pellets, sago waste, saltbush (Atriplex canescens) leaves, tree fern, rice husk ash and neem bark, grape stalk wastes, etc. Some of the advantages of using plant wastes for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability and easy regeneration. However, the application of untreated plant wastes as adsorbents can also bring several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant materials. The increase of the COD, BOD and TOC can cause depletion of oxygen content in water and can threaten the aquatic life. Therefore, plant wastes need to be modified or treated before being applied for the decontamination of heavy metals. A comparison of adsorption efficiency between chemically modified and unmodified adsorbents was also reported in literature [67].

In a conclusion, a wide range of low-cost adsorbents obtained from naturel and chemical sorbent or chemically modified plant wastes has been studied and most studies were focused on the removal of heavy metal ions such as Cd, Cu, Pb, Zn, Ni and Cr(VI) ions. The most common chemicals used for treatment of plant wastes are acids and bases. Chemically modified plant wastes vary greatly in their ability to adsorb heavy metal ions from solution. Chemical modification in general improved the adsorption capacity of adsorbents probably due to higher number of active binding sites after modification, better ion-exchange properties and formation of new functional groups that favours metal up-
take. Although chemically modified plant wastes can enhance the adsorption of heavy metal ions, the cost of chemicals used and methods of modification also have to be taken into consideration in order to produce ‘low-cost’ adsorbents.

Another option is using biological materials [4, 66-68, 76, 77]. Biomaterials of microbial and plant origin interact effectively with heavy metals. Metabolically inactive dead biomass due to their unique chemical composition sequesters metal ions and metal complexes from solution, which obviates the necessity to maintain special growth-supporting conditions. Metal-sorption by various types of biomaterials can find enormous applications for removing metals from solution and their recovery. Rather than searching thousands of microbial species for particular metal sequestering features, it is beneficial to look for biomasses that are readily available in large quantities to support potential demand. While choosing biomaterial for metal sorption, its origin is a major factor to be taken into account, which can come from (a) microorganisms as a by-product of fermentation industry, (b) organisms naturally available in large quantities in nature and (c) organisms cultivated or propagated for biosorption purposes using inexpensive media. Different non-living biomass types have been used to adsorb heavy metal ions from the environment. Seaweed, mold, bacteria, crab shells and yeast are among the different kinds of biomass, which have been tested for metal biosorption or removal. Advantages and disadvantages of biosorption by non-living biomass are as follows [67, 75-77]:

Advantages of biosorption;

1. Growth-independent, non-living biomass is not subject to toxicity limitation of cells. No requirement of costly nutrients required for the growth of cells in feed solutions. Therefore, the problems of disposal of surplus nutrients or metabolic products are not present.
2. Biomass can be procured from the existing fermentation industries, which is essentially a waste after fermentation.
3. The process is not governed by the physiological constraint of living microbial cells.
4. Because of non-living biomass behave as an ion exchanger; the process is very rapid and takes place between few minutes to few hours. Metal loading on biomass is often very high, leading to very efficient metal uptake.
5. Because cells are non-living, processing conditions are not restricted to those conducive for the growth of cells. In other words, a wider range of operating conditions such as pH, temperature and metal concentration is possible. No aseptic conditions are required for this process.
6. Metal can be desorbed readily and then recovered if the value and amount of metal recovered are significant and if the biomass is plentiful, metal-loaded biomass can be incinerated, thereby eliminating further treatment.

Disadvantages of biosorption;

1. Early saturation can be problem i.e. when metal interactive sites are occupied, metal desorption is necessary prior to further use, irrespective of the metal value.
2. The potential for biological process improvement (e.g. through genetic engineering of cells) is limited because cells are not metabolizing. Because production of the adsorptive agent occurs during pre-growth, there is no biological control over characteristic of biosorbent. This will be particularly true if waste biomass from a fermentation unit is being utilized.

3. There is no potential for biologically altering the metal valency state. For example less soluble forms or even for degradation of organometallic complexes. Metabolic independent processes can mediate the biological uptake of heavy metal cations. Biosorption offers an economically feasible technology for efficient removal and recovery of metal(s) from aqueous solution. The process of biosorption has many attractive features including the selective removal of metals over a broad range of pH and temperature, its rapid kinetics of adsorption and desorption and low capital and operation cost. Biosorbent can easily be produced using inexpensive growth media or obtained as a by-product from industry. It is desirable to develop biosorbents with a wide range of metal affinities that can remove a variety of metal cations. These will be particularly useful for industrial effluents, which carry more than one type of metals. Alternatively a mixture of non-living biomass consisting of more than one type of microorganisms can be employed as biosorbents. Bacterial biomass, algal biomass, fungal biomass were applied to removal of metals in the waste waters. The use of immobilized biomass rather than native biomass has been recommended for large-scale application but various immobilization techniques have yet to be thoroughly investigated for ease, efficacy and cost effectiveness [67, 77].

Biosorption processes are applicable to effluents containing low concentrations of heavy metals for an extended period. This aspect makes it even more attractive for treatment of dilute effluent that originates either from an industrial plant or from the primary wastewater treatment facility. Thus biomass-based technologies need not necessarily replace the conventional treatment routes but may complement them. At present, information on different biosorbent materials is inadequate to accurately define the parameters for process scale up and design perfection including reliability and economic feasibility. To provide an economically viable treatment, the appropriate choice of biomass and proper operational conditions has to be identified. To predict the difference between the uptake capacities of the biomass, the experimental results should be tested against an adsorption model. The development of a packed bed or fluidized-bed biosorption model would be helpful for evaluating industrial-scale biosorption column performance, based on laboratory scale experiments and to understand the basic mechanism involved in order to develop better and effective biosorbent.

5. Conclusion

An unfortunate consequence of industrialization and industrial production is the generation and release of toxic waste products which are polluting our environment. Many trace and heavy metals (Cd, Pb, Mn, Cu, Zn, Cr, Fe and Ni) and their compounds have been found that are toxic. Many of them are used in several industrial activities including metallurgy,
tanneries, petroleum refining, electroplating, textiles and in pigments. Their presence in environment has been responsible for several types of health problems in animals, plants and human beings. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whilst the direct discharge into the sewerage system may affect negatively.

The analysis of wastewater for trace and heavy metal contamination is an important step in ensuring human and environmental health. Wastewater is regulated differently in different countries, but the goal is to minimize the pollution introduced into natural waterways. In recent years, metal production emissions have decreased in many countries due to legislation, improved cleaning technology and altered industrial activities. Today and in the future, dissipate losses from consumption of various metal containing goods are of most concern. Therefore, wastewater may need to be measured for a variety of metals at different concentrations, in different wastewater matrices. A variety of inorganic techniques can be used to measure trace elements in waste water including atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and ICP mass spectrometry (ICP-MS). Depending upon the number of elements that need to be determined and the number of samples that need to be run, the most suitable technique for business requirements can be chosen.

Several industrial wastewater streams may contain heavy metals such as Cd, Sb, Cr, Cu, Pb, Zn, Co, Ni, etc. The toxic metals, probably existing in high or even in low concentrations, must be effectively treated/removed from the wastewaters. The various treatment methods employed to remove heavy or trace metals, adsorption and chemical precipitation process is the most common treatment technology. The conventional heavy metal removal process has some inherent shortcomings such as requiring a large area of land, a sludge dewatering facility, skillful operators and multiple basin configuration. In recent years, some new processes have been developed for the heavy metal removal from wastewater, like biosorption, neutralization, precipitation, ion exchange etc. The use of all these techniques for removal of the heavy metals offers several advantages and limitations compared to each other. The important parameters for the selection of removal technique of heavy metal from waste water are waste type, the growth of the wastewater field, cheap or low-cost removal material, operational costs and problem of disposal of residual metal sludge. The significance of developing new treatment/removal methods for heavy metal from waste or waste water samples has been widely recognized especially in the fields of environmental sciences.

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